TRANSITION METAL COMPLEXES WITH POLYAMINE LIGANDS

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A. Ross Gainsford

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ABSTRACT

Tri and pentaaminecobalt (III) complexes of various linear and substituted polyamine ligands have been studied.

A series of complexes of the type trans - Co $(ABA)X_3$ (ABA = tridentate linear polyamine = dien, 2,3-tri, dpt or 4-dodec-dien) have been prepared in an investigation to determine the extent to which ring size influences the stereochemistry of the faculative ligands.

The preparation of μ-peroxodicobalt (III) decaamine perchlorates, $[Co_2(AA)_2(ABA)_2O_2](ClO_4)_4 \cdot xH_2O$, and their decomposition with $HCl/ZnCl_2$ solution to form isomeric complexes of the form $Co(AA)(ABA)Cl^{2+}$ (AA = bidentate linear polyamine = en, pn, ibn, tmd; ABA = tridentate linear polyamine = dien, 2,3-tri or dpt) has been investigated.

The reaction of complexes of the type trans - $Co(ABA)X_3$ (ABA = tridentate linear polyamine = dien, 2,3-tri or dpt) with linear diamines (en, pn, ibn, tmd, Me-tmd, Bu-tmd, tmd-hex, Nip-ibn or stien) has also been used as an efficient method of preparing isomeric $Co(AA)(ABA)Cl^{2+}$ complexes.

Using the above and other reaction routes, the following number of isomers (in parenthesis) have been synthesised; $Co(en)(dien)Cl^{2+}$ (3), $Co(pn)(dien)Cl^{2+}$ (7), $Co(ibn)(dien)Cl^{2+}$(7), $Co(stien)(dien)Cl^{2+}$ (4),

$Co(tmd)(dien)\ Cl^{2+}$ (7), $Co(Me\text{-}tmd)(dien)Cl^{2+}$ (5), $Co(Bu\text{-}tmd)(dien)Cl^{2+}$ (2), $Co(tmd\text{-}hex)(dien)Cl^{2+}$ (2), $Co(Nip\text{-}ibn)(dien)Cl^{2+}$ (5), $Co(1,4\text{-}bn)(dien)Cl^{2+}$ (1), $Co(2,3\text{-}tri)(en)Cl^{2+}$ (2), $Co(en)(dpt)Cl^{2+}$ (2), $Co(pn)(dpt)Cl^{2+}$ (4), $Co(ibn)(dpt)Cl^{2+}$ (4) and $Co(tmd)(dpt)Cl^{2+}$ (6).

Various isomeric acidopentaaminecobalt (III) complexes have been derived from the isomeric chloro complexes obtained from the above reactions.

All complexes have been characterised by their infrared and visible absorption spectra. In addition, crystallographic space groups and unit cell dimensions of some isomers have been determined.

The crystal structures of the π and *K* isomers of $[Co(en)(dien)Cl]ZnCl_4$ have been determined.

For the π isomer, the three nitrogens of the diethylenetriamine ligand are in a facial configuration and the chlorine atom occupies one of the two equivalent <u>cis</u> positions relative to the coordinated secondary amine group of the diethylenetriamine. The ethylenediamine ligand occupies the remaining two coordination positions.

For the *K* isomer, the three nitrogen atoms of the diethylenetriamine ligand are in a plane with one nitrogen atom of the ethylenediamine ligand, while the second ethylenediamine nitrogen atom is <u>trans</u> to the chlorine atom.

The orientation about the secondary nitrogen group of the diethylenetriamine ligand is such that the NH proton is remote from the coordinated chlorine atom.

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ABBREVIATIONS

The following abbreviations are used in this thesis:

tetren = tetraethylenepentamine = $NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$.

penten = N, N, N', N'-tetrakis-(2-aminoethyl)-ethylenediamine = $[NH_2(CH_2)_2]_2N(CH_2)_2N[(CH_2)_2NH_2]_2$.

trenen = 4-(2-aminoethyl)-1,4,7,10-tetraazadecane = $NH_2(CH_2)_2N[(CH_2)_2NH_2](CH_2)_2NH(CH_2)_2NH_2$.

Metrenen = 4-(2-aminoethyl)-7-methyl-1,4,7,10-tetraazadecane = $NH_2(CH_2)_2N[(CH_2)_2NH_2](CH_2)_2N[CH_3](CH_2)_2NH_2$.

trien = triethylenetetramine = $NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$.

dien = diethylenetriamine = $NH_2(CH_2)_2NH(CH_2)_2NH_2$

2,3-tri = 1,4,8-triazaoctane = $NH_2(CH_2)_2NH(CH_2)_3NH_2$.

dpt = dipropylenetriamine = $NH_2(CH_2)_3NH(CH_2)_3NH_2$.

en = ethylenediamine = $NH_2(CH_2)_2NH_2$

pn = (d,l)-1,2-propanediamine = $NH_2CH_2CH(CH_3)NH_2$.

ibn = isobutylenediamine = $NH_2CH_2C(CH_3)_2NH_2$

Nip-ibn = N^1-isopropyl-2-methyl-1,2-propanediamine = $(CH_3)_2[CH]NHC(CH_3)_2CH_2NH_2$.

stien = meso-stilbenediamine = $NH_2(CH\emptyset)_2NH_2$.

tmd = 1,3-propanediamine = $NH_2(CH_2)_3NH_2$.

Me-tmd = N-methyl-1,3-propanediamine = $(CH_3)NH(CH_2)_3NH_2$

Bu-tmd = N-(n-Butyl)-1,3-propanediamine = $(C_4H_9)NH(CH_2)_3NH_2$

tmd-hex = N-cyclohexyl-1,3-propanediamine = $(C_6H_{11})NH(CH_2)_3NH_2$.

1,4-bn = 1,4-butanediamine = $NH_2(CH_2)_4NH_2$.

$\underline{d}_6$-DMSO = Deuterated dimethylsulphoxide = $(CD_3)_2SO$.

DMF = N,N-Dimethylformamide = $(CH_3)_2NCOH$.

TMS = Tetramethylsilane = $(CH_3)_4Si$.

ϕ = Ph = Phenyl group = C_6H_5- .

gly = glycine = $NH_2CH_2CO_2H$.

dmg = dimethylglyoxime = $[(CH_3)CN(OH)]_2$.

acac = acetylacetone = $(CH_3)CO(CH_2)CO(CH_3)$.

$\underline{F}$ - Formality = Formal Concentration.

4-dodec-dien = 4-dodecyl-diethylenetriamine

= $CH_3(CH_2)_{11}N[(CH_2)_2NH_2](CH_2)_2NH_2$

I N T R O D U C T I O N

INTRODUCTION

This research has involved, primarily, the preparation, characterisation and structural assignments of the isomers formed by different configurations that linear polyamines can adopt in mixed triamine-diamine cobalt (III) systems. The isomerisations produced by change of acido ligand at the sixth coordination site around the cobalt (III) atom has been studied.

Another point of interest in this study is the influence on the type of isomers that can be formed with change of ring size in the diamine and triamine ligands.

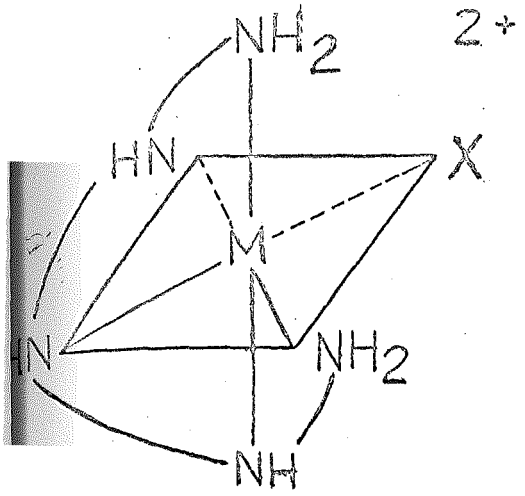
Coordination complexes containing cobalt have been the most extensively employed for theoretical studies. The complex ions of cobalt are generally more stable and more easily prepared than those of other metals, which permits more detailed investigation of isomerisation reactions and reaction mechanisms than otherwise would be possible.

The most stable coordination complexes of cobalt are those in which the covalently bonded species contain electronegative atoms, e.g. nitrogen and oxygen, which are capable of forming bonds with the cobalt ions by donation of electron pairs. The nitrogen atoms of ammonia and organic amines form bonds especially well with cobalt ions.

When the majority of the coordinated ligands are ammonia or amines, oxidation of cobalt (II) to cobalt (III) occurs readily. Because the ammonia or amine molecules are strong electron donors in forming the coordinate bonds, the removal of the electron from cobalt (II) is facilitated by the strong donation of pairs of electrons to cobalt by the amines. The product of the oxidation is much more stable than the original cobalt (II) complex.

Chloropentaaminecobalt (III) cations of the type $Co(NH_3)_5Cl^{2+}$ [1,2] and *cis*[3,4] and *trans*[5,6] - $Co(en)_2NH_3Cl^{2+}$ have been known for a long time. Ethylenediamine, a representative polyamine is a regularly behaving, strongly coordinating chelate ligand which acts very much like two coordinated ammonia molecules and many complexes of the *cis* - $Co(en)_2ACl^{2+}$ (A = monoamine) type are known[7]. Recently, however, interest has centred on the use of multidentate linear polyamines, e.g. tetren, which can form a variety of geometric isomers.

In 1955, Boston, Basolo and Pearson[8] prepared a non-crystalline material which had a chlorine analysis agreeing with the formula $[Co(tetren)Cl]Cl_2$ within 1-2%. From a study of its aquation kinetics it was deduced that the material contained 51% of a "slow" component, which was taken to be an isomer of the above compound (later[9] written without comment as isomer I, Fig. 1) and 49% of a "fast" component which was



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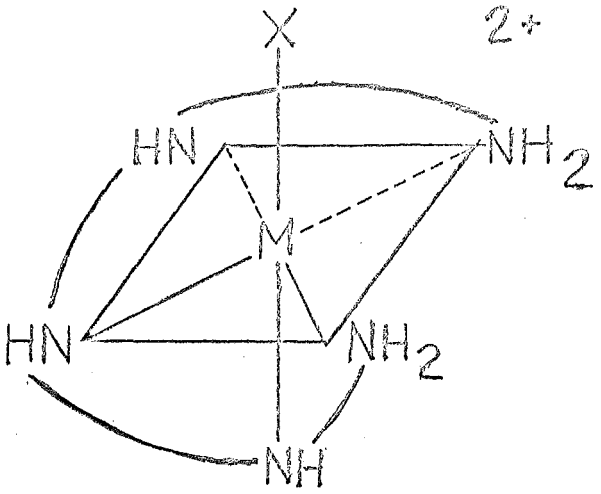

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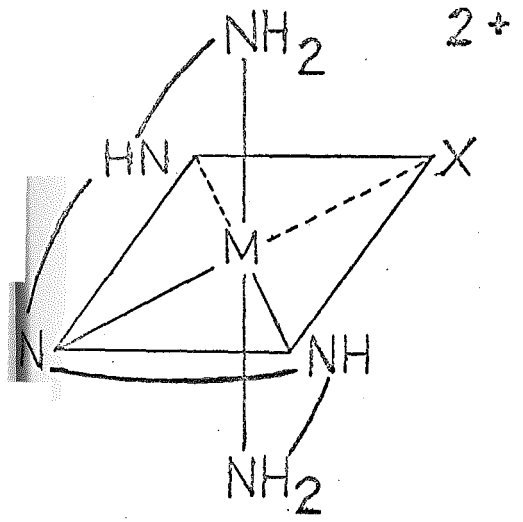
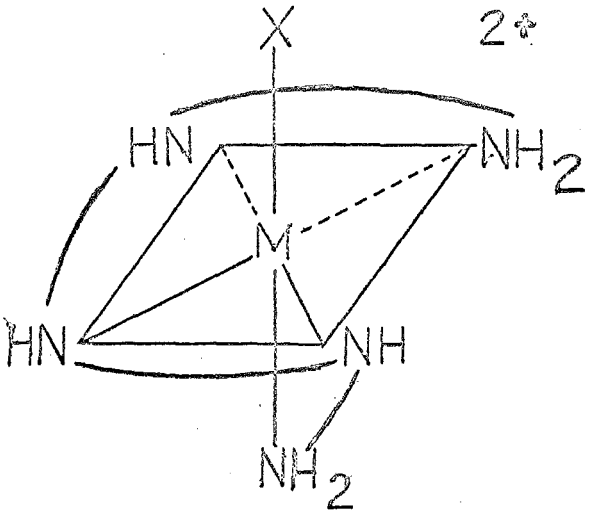


III



IV

Figure 1. Possible Geometric Isomers of $Co(tetren)X^{2+}$.

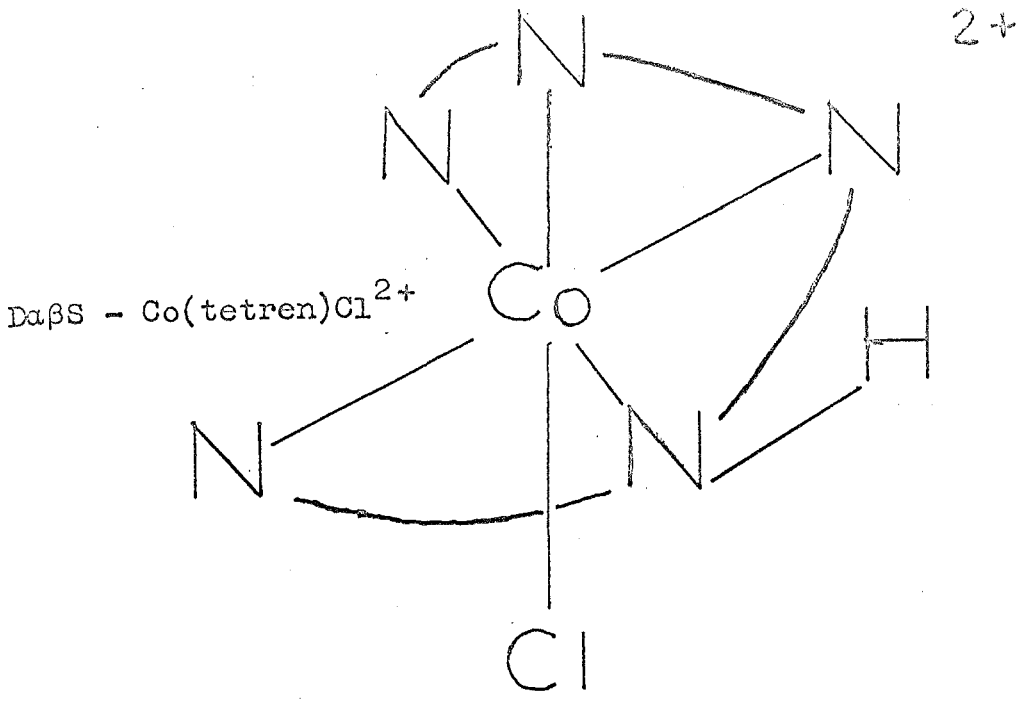
assumed to be more likely a "dichloro tertiary pentamine complex".

Using a synthesis similar to that used above, but using purified tetren[10], Fraser[11] obtained a "$[Co(tetren)Cl](ClO_4)_2$" (no analytical data given) which, on reduction with V^{2+} or Cr^{2+} (apparently in 1 F $HClO_4$), gave rate plots showing a "fast" and a "slow" component present in approximately equal amounts. It was suggested that these were $Co(tetren)Cl^{2+}$ isomers and a tentative assignment of their configuration as III and IV, Fig. 1, was made.

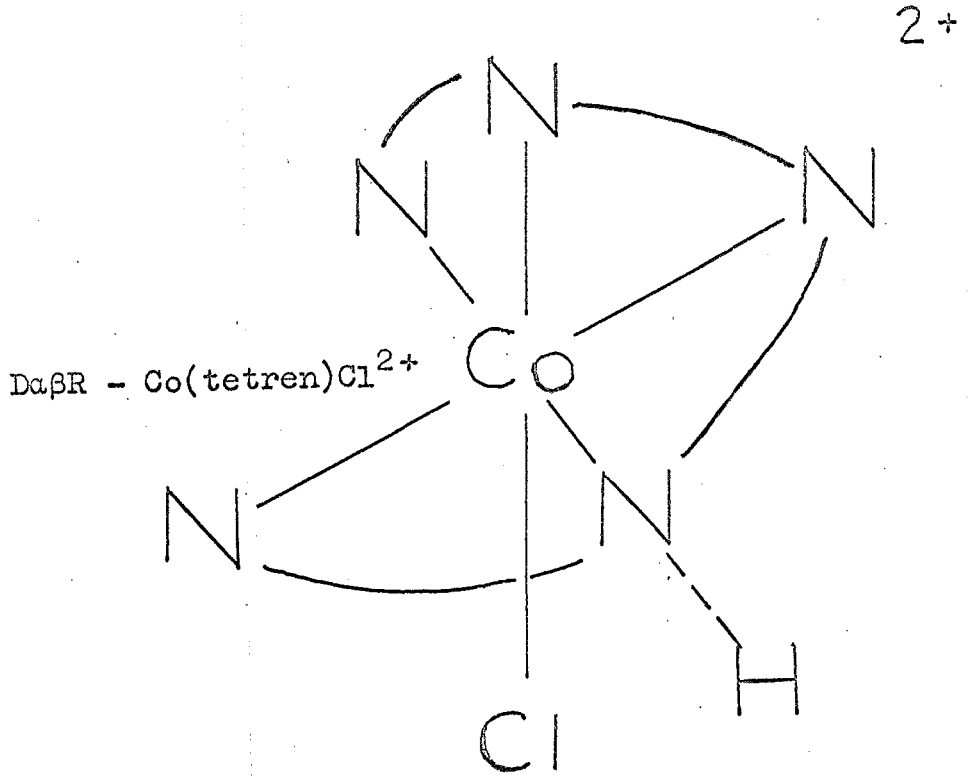
Mark and Anson[11a] have also reported the synthesis of a "$Co(tetren)Br^{2+}$" but no structural assignments were made.

House and Garner,[12,13] by the use of a series of different synthetic methods and utilising the solubility properties of the tetrachlorozincate (II) anion, isolated two isomers α and β, which they assigned structures I and II, Fig. 1, respectively.

At about the same time, Buckingham, Sargeson and Marzilli[14] prepared four isomers analysing for [Co(tetren)Cl]X including those of House and Garner. The single crystal structures of these have been determined.[15-17] The DαβR (equivalent to the House and Garner Dα isomer) and DαβS (equivalent to the House and Garner racemic β isomer) were found to be related by proton inversion (Fig. 1A) at the "planar" secondary nitrogen atom of the tetren ligand in isomer II, Fig. 1.[15]



Dαβ S - Co(tetren)Cl^{2+}



Dαβ R - Co(tetren)Cl^{2+}

Figure 1A. Structures of Dαβ S and Dαβ R - Co(tetren)Cl^{2+}.

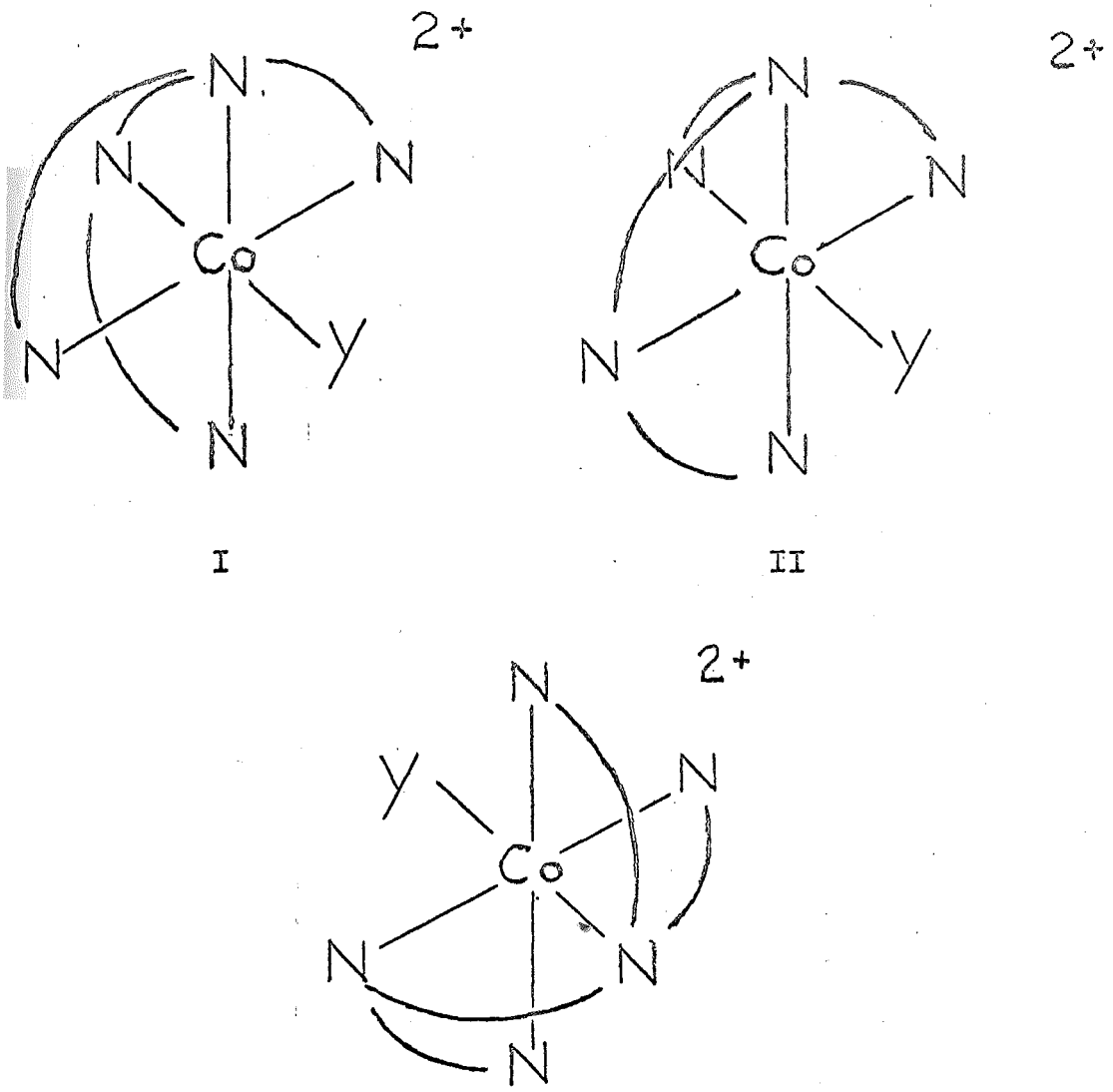


Figure 2. Possible Geometric Isomers of $Co(trenen)Y^{2+}$.

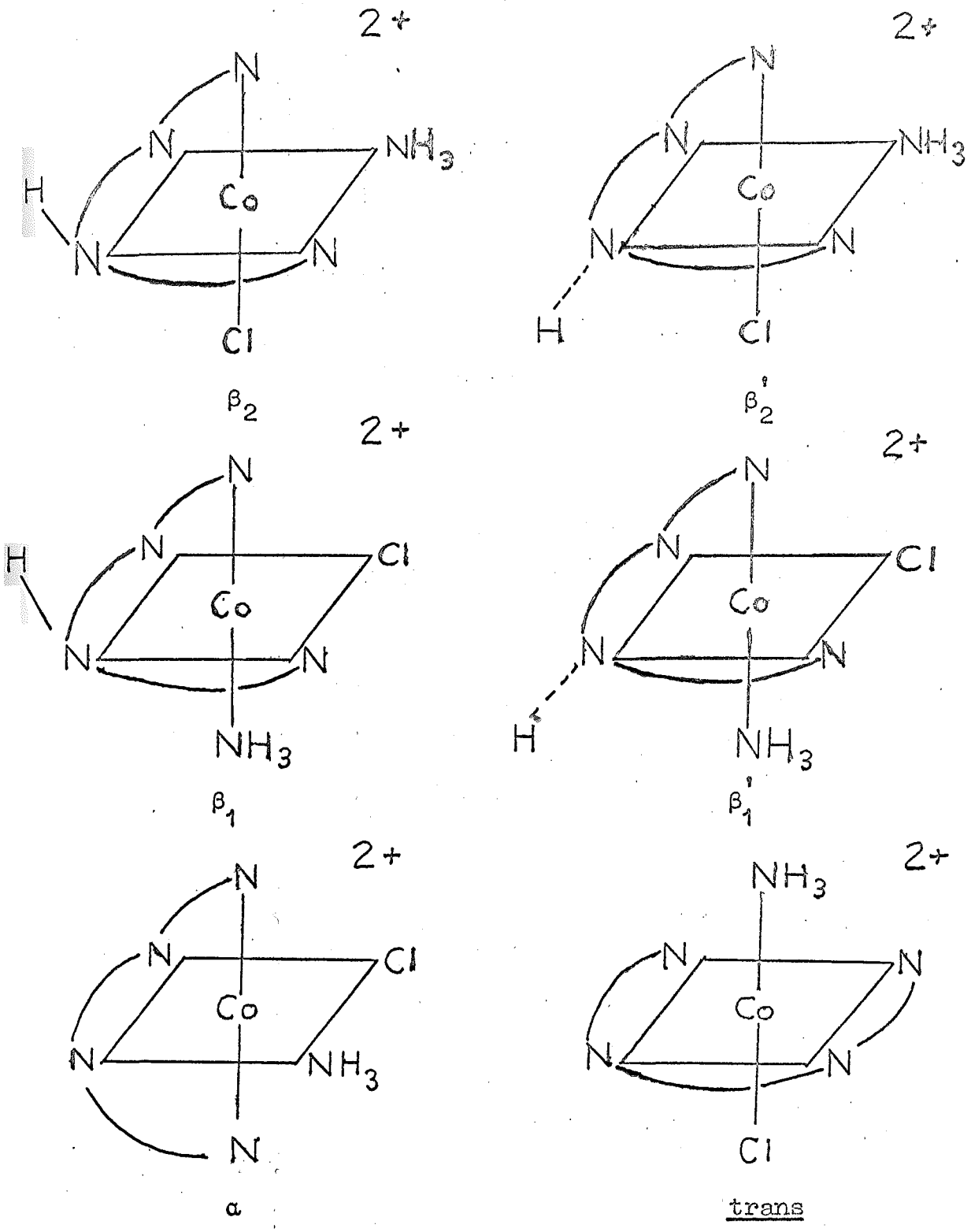


Figure 3. Possible Geometric Isomers of $Co(trien)NH_3Cl^{2+}$.

The αα isomer[16] was found to correspond to isomer I, Fig. 1, and the fourth isomer proved to be a complex of the branched polyamine, trenen[17], isomer I, Fig. 2.

It is now apparent that of the potentially nine isomers of $Co(tetren)Cl^{2+}$, only three (α = αβR, β = αβS and αα) have been isolated.

Complexes of the potentially hexadentate ligand, penten, have been reported by Emmenegger and Schwarzenbach.[18] They have also reported a series of compounds of the type $Co(H\ penten)X^{n+}$ where H penten represents this ligand coordinated through only five of its donor nitrogen atoms while the sixth is protonated. Complexes where $X = F^-$, Cl^-, Br^-, I^-, SCN^-, NO_2^-, CO_3^{2-}, $C_2O_4^{2-}$, $SO_4^=$ and H_2O have been prepared.

In 1967, Sargeson and Searle[19] first reported the synthesis of isomeric complexes of diacidotriethylenetetraminecobalt (III) ions.

The related chloroamminetriethylenetetraminecobalt (III) system reported by Gainsford and House[20] has been studied in detail by Dwyer[21]. Three isomeric complexes were synthesised, two of these (α and β_2) by reacting the $Co_2(trien)_2(NH_3)_2O_2^{4+}$ cation with $HCl/ZnCl_2$ and the third (β_2') by chromatographic separation of the product obtained by base hydrolysis and reanation in HCl of the β_2 isomer (Fig. 3). Dwyer also prepared one isomer of $Co(Metrenen)Cl^{2+}$

but this does not have the same configuration as the sym - $Co(trenen)Cl^{2+}$ isomer obtained by Buckingham *et al*.[17,21]

Both acid and base hydrolysis kinetics were studied for the three $Co(trien)NH_3Cl^{2+}$ isomers and the single crystal structure of the α (racemic) isomer was determined (Fig. 4).[22]

In the $Co(AA)(ABA)Cl^{2+}$ system, Boston, Basolo and Pearson[8] prepared "$[Co(en)(dien)Cl]Cl_2$" and studied its hydrolysis in aqueous acidic media. However, no further data was offered on this complex.

In 1966, Bosnich and Dwyer[23,24] re-examined the $Co(en)(dien)Cl^{2+}$ system. They prepared two isomers (ω and ε) by the reaction of ethylenediamine with *trans*-trinitro(diethylenetriamine)cobalt (III) and also by the reaction of diethylenetriamine with *trans*-trinitro-ammineethylenediaminecobalt (III). A series of complexes containing the acido ligands Cl^-, Br^-, I^-, NCS^- and NO_3^- having the same configuration as the ω isomer were also synthesised. The ω and ε isomers were tentatively assigned to isomers I and III, (no distinction as to the configuration at "planar" secondary amine) respectively, in Fig. 5. The kinetics of acid hydrolysis of the two chloro isomers and also the bromo and iodo complexes was also studied[24].

From a single crystal X-ray analysis the ω isomer (as the dichloride hemihydrate salt) has been shown by Johnston[25,26] to have the geometric configuration II, Fig.5.

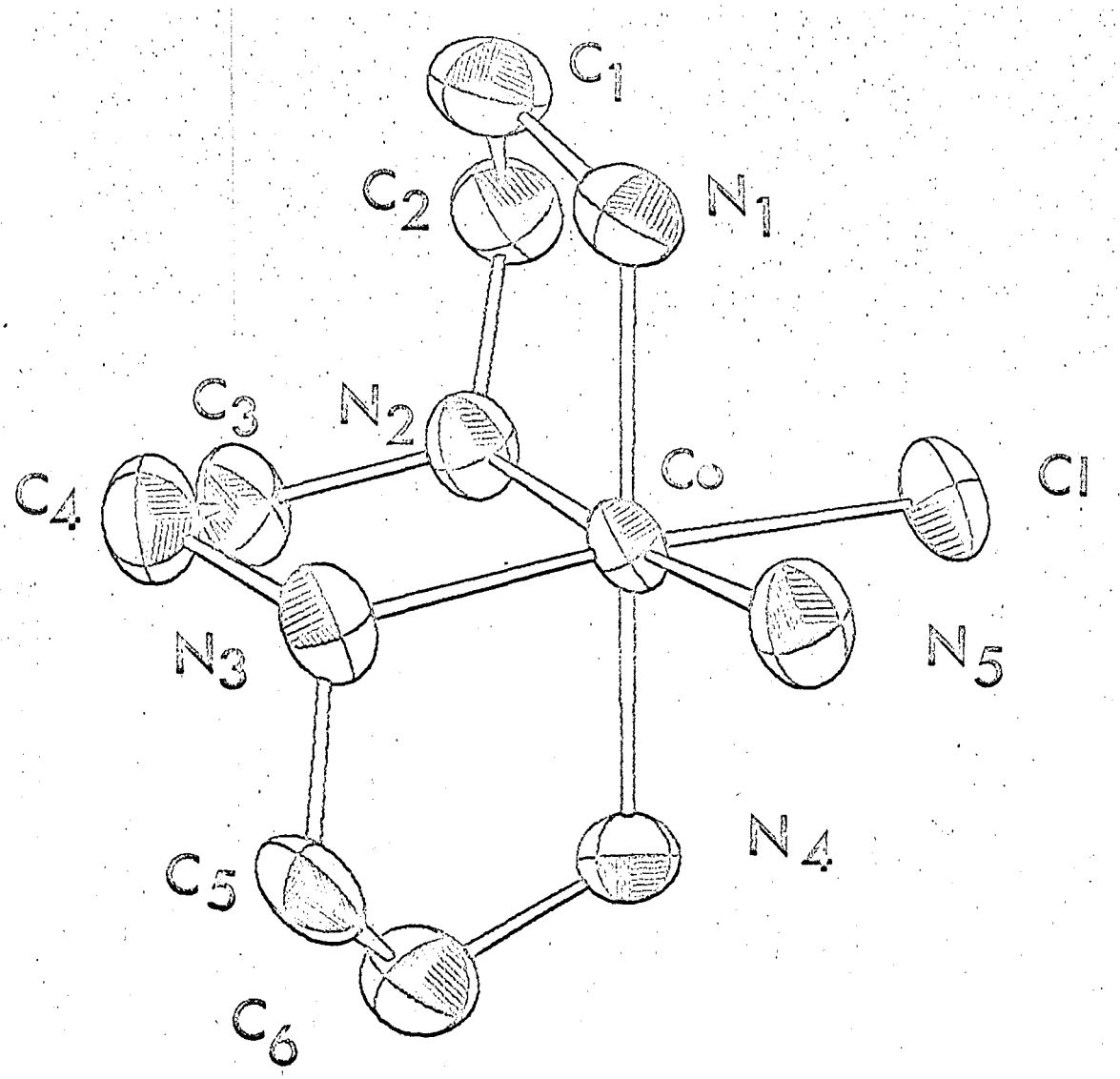
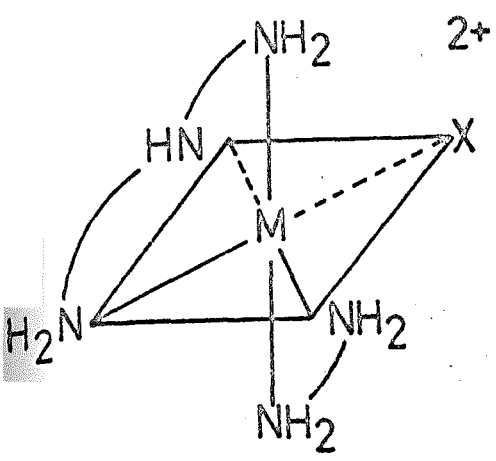


Figure 4. Perspective view of α-$[Co(trien)NH_3Cl]^{2+}$ cation.



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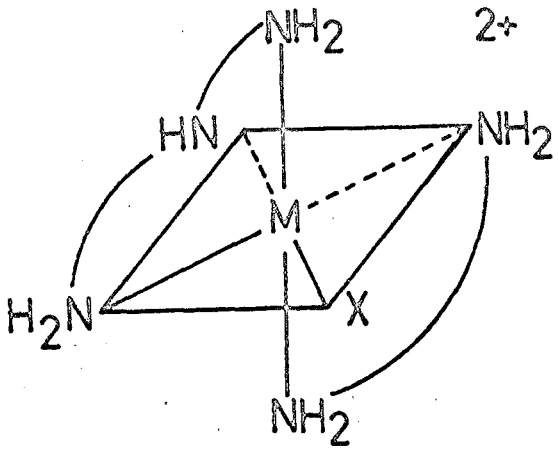

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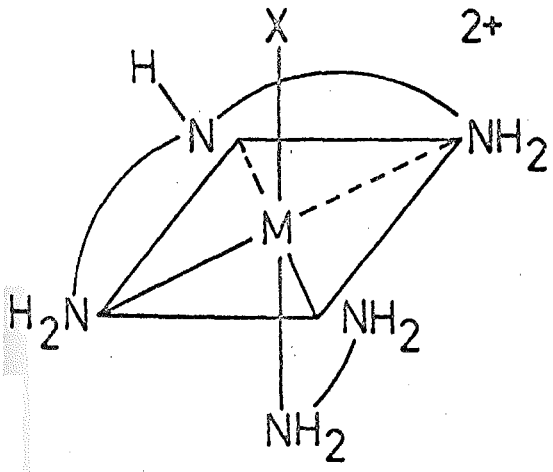
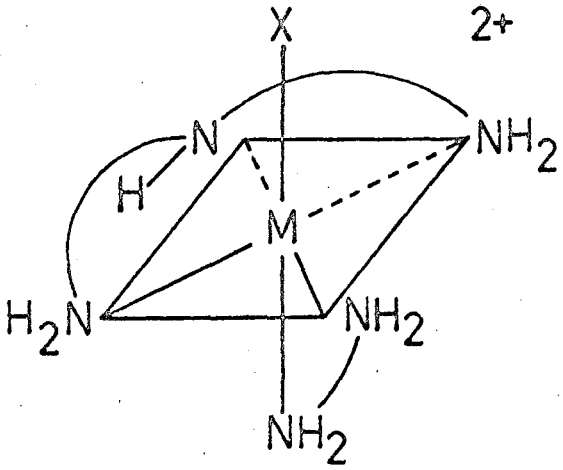


IIIa



IIIb

Figure 5. Possible geometric isomers in a $M(AA)(ABA)X^{2+}$ cation (AA = bidentate linear polyamine, ABA = tridentate linear polyamine).

In 1968, Beaumont[27] reported the preparation of $Co_2(en)_2(dien)_2O_2^{4+}$ to study the chemical and physical properties of peroxide bridged species in aqueous solution. However, no structural assignments were made as to the configurations within the μ-peroxo dicobalt (III) complex or in the products of its decomposition in HCl and in HBr.

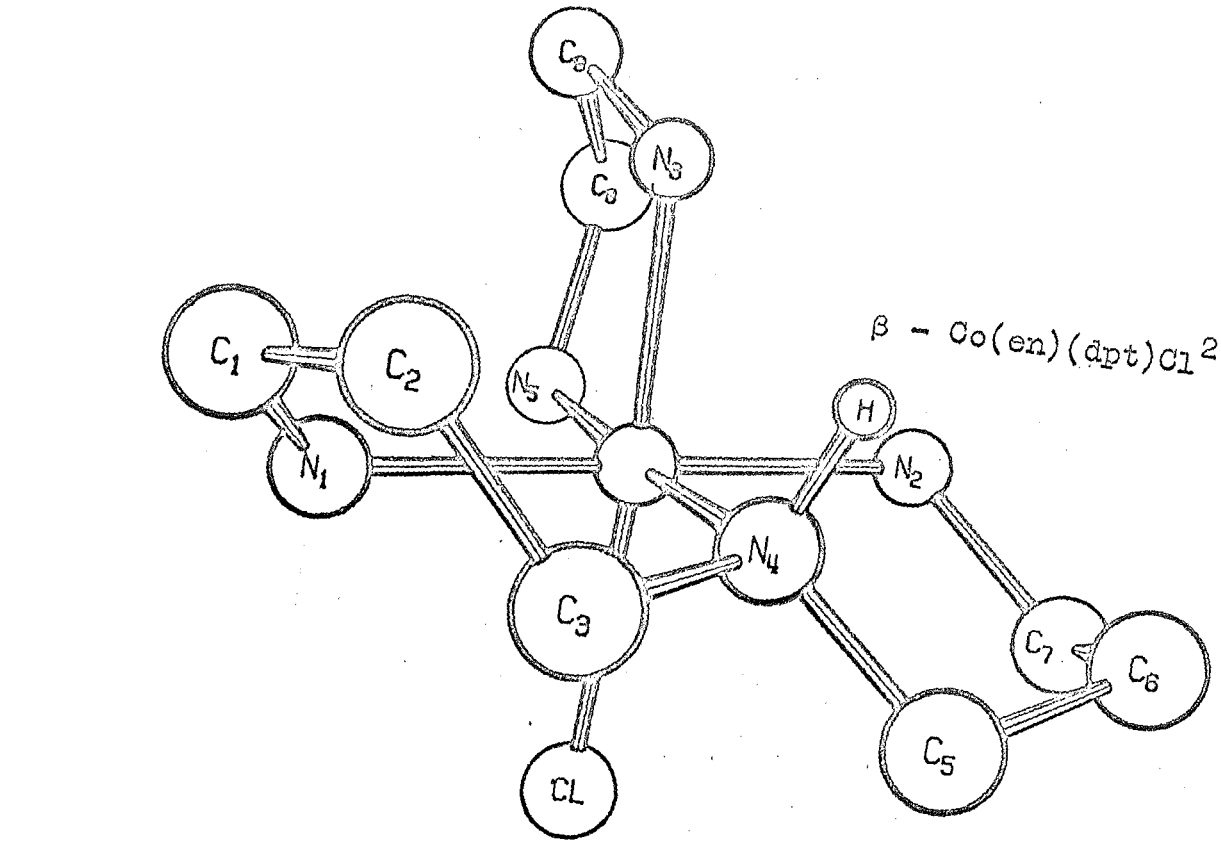
Schlessinger[28] has extended the data for the mixed triamine-diamine systems by preparing $Co(en)(dien)Cl^{2+}$ (1 isomer), $Co(pn)(dien)Cl^{2+}$ (1 isomer), $Co(tmd)(dien)Cl^{2+}$ (1 isomer), $Co(en)(dpt)Cl^{2+}$ (1 isomer) and $Co(pn)(dpt)Cl^{2+}$ (1 isomer through the reaction of a trinitrotriaminecobalt (III) complex with a diamine. Again no structural assignments were made.

In 1969, Gainsford and House[29,30] reported the synthesis of three isomers, α, β and γ, of the $Co(en)(dpt)Cl^{2}$. A series of isomeric complexes $Co(en)(dpt)X^{n+}$ where X = Br^-, I^-, N_3^-, NCS^- and OH_2 were also prepared. The γ isomer has recently[31] been shown to consist of a constant composition crystallising mixture of 73% α-$[Co(en)(dpt)Cl]ZnCl_4$ and 27% α-$[Co(en)(dpt)NO_2]ZnCl_4$ (previously assigned as γ-$[Co(en)(dpt)NO_2]ZnCl_4$). The α, β and "γ" isomers were tentatively assigned to structures I, III and II, fig. 5, respectively. There was no distinction as to the configuration of the proton at the "planar" secondary amine in the β isomer. In order to confirm these assignments, Ireland[32,33,34]

determined the single crystal structures of β-[Co(en)(dpt)Cl]$ZnCl_4$ and α-[Co(en)(dpt)Cl]$I_2.H_2O$ (Fig. 6). He found that the cobalt atoms are surrounded by one chlorine atom and five nitrogen atoms in an approximately octahedral configuration. For both cations the three nitrogen atoms of the dipropylenetriamine ligand are in a plane with one nitrogen atom of the ethylenediamine while the second nitrogen atom is <u>trans</u> to the chlorine atom . The orientation about the coordinated secondary amine nitrogen is such that the NH proton is, in the α isomer, adjacent to the chlorine atom (structure IIIa, Fig. 5) while in the β isomer it is remote from the chloride (structure IIIb, Fig. 5). Strain energy minimisation calculations[34] on these complexes have been performed and the predictions from these calculations have been confirmed by the observed crystal structures. The difference between the α and β isomers of $Co(en)(dpt)Cl^{2+}$ (Fig. 6) is the same as that encountered in the DαβR and DαβS isomers[15] of $(Co(tetren)Cl^{2+}$ and the β_2 and β_2' isomers[21] of $Co(trien)NH_3Cl^{2+}$.

<u>Reaction Rates</u>

Rates of acido ligand release, both in acidic and basic solution have been studied for several of the complexes described in this thesis. Preliminary base hydrolysis of α and β-$Co(en)(dpt)Cl^{2+}$ and of ω, π and *K* (equivalent to Bosnich and Dwyer's ε isomer[23,24]) -



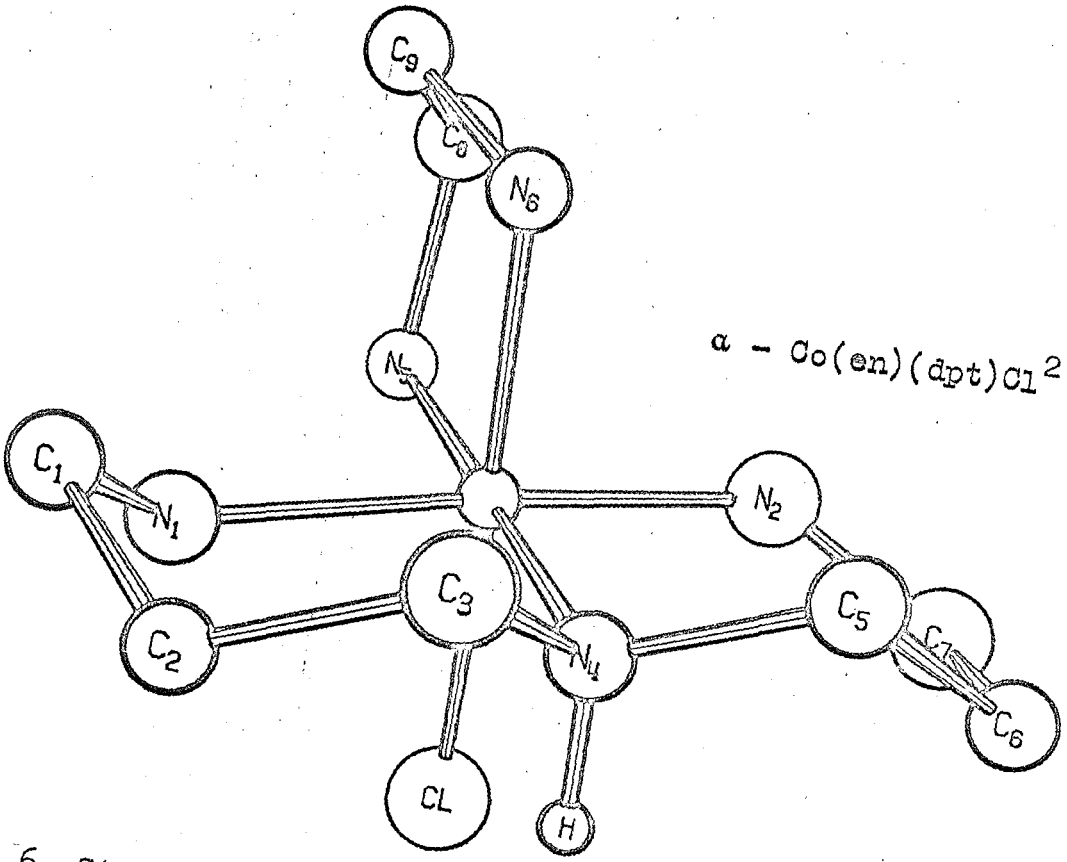


Figure 6. Structures of α and β - Co(en)(dpt)Cl 2+ Cations.

$Co(en)(dien)Cl^{2+}$ have been carried out by Hay[35]. The results that he has obtained together with those obtained by Dwyer[21] for the α, β_2 and β_2' isomers of $Co(trien)CH_3Cl^{2+}$ and the $Co(Metrenen)^{2+}$ isomer, Buckingham *et al*. for *sym* - $Co(trenen)Cl^{2+}$, and Ni and Garner[36] for the α and β isomers of $Co(tetren)Cl^{2+}$ are summarised in Table 1. The base hydrolysis rates appear to be sensitive to stereochemistry. It appears that any complex containing a "planar" secondary amine cis to the coordinated chloride will base hydrolyse at a rate several orders of magnitude greater than those complexes that do not contain this feature in their configurations.

The kinetics of acid aquation on the ω, π and *K* isomers of $Co(en)(dien)Cl^{2+}$ has been investigated by Tee[37] and the kinetics of Mercury (II) catalysed aquation on the same complexes has been been investigated by Mulvihill[38]. The results obtained, together with those of α and β-$Co(tetren)Cl^{2+}$ [36] and the earlier work by Bosnich and Dwyer[24] on the ω and $\varepsilon(K)$ isomers of $Co(en)(dien)X^{2+}$ ions are listed in Table 1. From this limited amount of data, it appears that aquation rates (replacement of Cl^- by H_2O in acid solution) are rather insensitive to stereochemistry. Tee[37] has also made preliminary studies on the acid aquation of the α and β isomers of $Co(en)(dpt)Cl^{2+}$.

Table 1

Kinetic Data for some Chloropentaaminecobalt(III) Complexes with Polyamine Ligands

A. Base Hydrolysis at 25°

Cation	Structure	Medium pH	Medium μ	$k(M^{-1}sec^{-1})$	Reference
α-Co(tetren)Cl^{2+}	Fig.1A	v	1	5.7×10^6	36
β-Co(tetren)Cl^{2+}	Fig.1A	v	1	1.7×10^6	36
sym-Co(tetren)Cl^{2+}	Fig.2,I.	8.03	1	885	17
Co(Metrenen)Cl^{2+}	Fig.2,III.[a]	9.05	1	27	21
α-Co(trien)$(NH_3)Cl^{2+}$	Fig.3	10.85	1	10.7	21
β_2-Co(trien)$NH_3)Cl^{2+}$	Fig.3	8.13	1	4.8×10^4	21
β_2-Co(trien)$(NH_3)Cl^{2+}$	Fig.3	5.49	1	2.3×10^5	21
ω-Co(en)(dien)Cl^{2+}	Fig.5,II	9.60	0.1	7.25	35
π-Co(en)(dien)Cl^{2+}	Fig.5, I	9.40	0.1	362	35
κ-Co(en)(dien)Cl^{2+}	Fig.5,IIIb	6.0	0.1	4.7×10^4	35
α-Co(en)(dpt)Cl^{2+}	Fig.5,IIIa	6.60	0.1	8.6×10^3	35
β-Co(en)(dpt)Cl^{2+}	Fig.5,IIIb	6.60	0.1	2.2×10^3	35

v variable pH

a Me group not shown in Fig. 2

B. Acid Hydrolysis[c]

Cation	Structure	T(°C)	$10^5 k(sec^{-1})$	Ea	Reference
α-Co(tetren)Cl^{2+}	Fig.1A	70	2.2	27	36
β-Co(tetren)Cl^{2+}	Fig.1A	70	1.3	29	36
ω-Co(en)(dien)Cl^{2+}	Fig.5,II	70	3.74	24.3	37
π-Co(en)(dien)Cl^{2+}	Fig.5,I	70	8.89	25.0	37
ϰ-Co(en)(dien)Cl^{2+}	Fig.5,IIIb	70	4.28	24.6	37
α-Co(en)(dpt)Cl^{2+}	Fig.5,IIIa	55	7.93	-	37
β-Co(en)(dpt)Cl^{2+}	Fig.5,IIIb	55	69.75	-	37

[c] μ = 1, 1 F $HClO_4$

C. Hg^{2+} Catalysed Aquation [d]

Cation	Structure	T(°C)	$10^3 k(M^{-1}sec^{-1})$	Ea	Reference
$Co(NH_3)_5Cl^{2+}$ [e]		25	113		38
ω-Co(en)(dien)Cl^{2+} [e]	Fig.5,II	25,35	4.87,13.3	17.7	38
π-Co(en)(dien)Cl^{2+} [e]	Fig.5,I	25,35	15.6,31.5	12.2	38
ϰ-Co(en)(dien)Cl^{2+} [e]	Fig.5,IIIb	25,35	5.11,15.3	19.5	38

[d] μ = 1, 1 F $HClO_4$

[e] As the $ZnCl_4^{2-}$ salt

D. V^{2+} Catalysed Reduction at 25° [f]

Cation	Structure	$k(M^{-1}sec^{-1})$	Reference
α-Co(tetren)Cl^{2+}	Fig.1A	4.9	12
β-Co(tetren)Cl^{2+}	Fig.1A	8.3	12

[f] μ = 1, 1 F $HClO_4$

Other Physico-chemical studies

(1) Acid dissociation constants

Beaumont[39] has reported the acid dissociation constant for "Aquo(ethylenediamine)(diethylenetriamine) cobalt (III) Ion", $Co(en)(dien)OH_2^{3+}$, but possible isomers of this complex have been ignored. On an appraisal of the method that was used to generate this cation, it is apparent that the study has been performed on a mixture of the π and K isomers.

(2) Optical Activity

Although resolution of the optical isomers of $\alpha\beta R$ and $\alpha\beta S$ - $Co(tetren)Cl^{2+}$ [12,15] and β_2 and β_2'-$Co(trien)NH_3Cl^{2+}$ [21] can be easily effected, this is of little assistance to the assigning of the structures of these isomers since most of the isomers in these systems are potentially optically active. However, in a $Co(AA)(ABA)X^{n+}$ system (AA = linear unsubstituted bidentate, e.g. en; ABA = linear unsubstituted tridentate, e.g. dien), only one isomer is potentially optically active (structure I, Fig. 5) and thus the resolution of one of these types of complexes into its optical isomers automatically assigns the structure of that complex.

P R E A M B L E

PREAMBLE

Recently, reaction mechanisms in transition metal complexes have been studied in detail using the simple complexes $Co(NH_3)_5X^{n+}$ and *cis* and *trans* - $Co(AA)_2\ XY^{n+}$ (AA = bidentate linear diamine). However, isomeric complexes are required to follow the steric course of these reactions and only a limited number of these, whose structures are known, are available.

It was the purpose of this study to prepare a series of $Co(AA)(ABA)X^{n+}$ complexes and determine their structures with a view to them being used for kinetic studies. Within a particular system, the isomers have the advantage of constant metal ion, charge and inductive and electromeric effects, with only the stereochemistry being varied. A possible secondary effect is the use of the reaction rate as a means of structural elucidation.

C H A P T E R 1

μ-PEROXODICOBALT (III) DECAMINE COMPLEXES AND TRANS-TRIACIDO (TRIAMINE) COBALT (III) COMPLEXES

INTRODUCTION: μ-PEROXODICOBALT (III) DECAAMINE COMPLEXES

Cobalt (III) complexes containing peroxide bridges have been known since 1852 when the first was reported by Fremy[40]. Marquenne[41], Vortmann[42] and Werner[43] subsequently succeeded in preparing a number of compounds containing the cation $(NH_3)_5Co\ O_2\ Co(NH_3)_5^{4+}$.

Unpublished work from the University of Idaho, U.S.A., indicates the formation of peroxo-bridged complexes containing the ligands propylenediamine[45], ethylenediamine[46], diethylenetriamine[47], tetraethylenepentamine[48], 2-(2-aminoethyl) aminoethanol[49] and triethylenetetramine[50] but no solid compounds were isolated for analysis.

The $Co_2(NH_3)_{10}\ O_2^{4+}$ complex is characterised by its brown colour, diamagnetism and its instability in aqueous solution. Various workers have failed to find any solvent mixture in which the complex is completely stable[51-53].

The decomposition of this complex in acid solution has been studied by Charles and Barnartt[53]. Ion exchange techniques revealed that the decomposition gave 50% Co^{2+}, 8% $Co(NH_3)_6^{3+}$, 6.4% of the green superoxo complex $Co_2(NH_3)_{10}O_2^{5+}$ and the remainder (35.6%) as $Co(NH_3)_5OH_2^{3+}$. However, Rohm and Nyman[44] studied the same reaction but found that only Co^{2+}, O_2 and NH_4^+ were formed. Charles and Barnartt apparently used an aged peroxo complex and this may account

for the conflicting results obtained above.

In spite of the conflicting results in the acid decomposition of $Co_2(NH_3)_{10}O_2^{4+}$, we have found that the decomposition of several μ-peroxodicobalt (III) decamine perchlorate complexes results in the formation of acidopentaaminecobalt (III) complexes containing polyamine ligands in high yields.

μ-peroxodicobalt (III) Decaamine Complexes[20]

A number of chloropentaaminecobalt (III) tetrachlorozincate (II) salts (Table 1.1) have been prepared, in several geometric configurations, by reacting the corresponding μ-peroxodicobalt (III) decaamine perchlorates with $HCl/ZnCl_2$ solution.

The dark brown polyamine μ-peroxo intermediates were formed by oxidising an aqueous solution of hydrated cobalt (II) nitrate, sodium perchlorate and the polyamine (tetren) or polyamine mixture with molecular oxygen.

In the case of $[Co(en)(dpt)Cl]ZnCl_4$, for example, the two isomers isolated from the decomposition of $[Co_2(en)_2(dpt)_2O_2](ClO_4)_4.2H_2O$ with 3.6 F HCl containing $ZnCl_2$, are deposited successively on evaporation of the solution.

The geometric isomers of the chloropentaaminecobalt (III) complexes listed in Table 1.1 have been characterised

Table 1.1

Complex [a]	Number of isomers isolated	
	Previous Work	This Work
$[Co(tetren)Cl]ZnCl_4$	2[8,12]; 4[14]	b
$[Co(en)(dien)Cl]ZnCl_4$	1[8,28]; 2[23,24]	2
$[Co(en)(dpt)Cl]ZnCl_4$	1[28]	2
$[Co(tmd)(dien)Cl]ZnCl_4$	1[28]	5
$[Co(tmd)(dpt)Cl]ZnCl_4$		6
$[Co(pn)(dien)Cl]ZnCl_4$	1[28]	5
$[Co(pn)(dpt)Cl]ZnCl_4$	1[28]	4
$[Co(ibn)(dien)Cl]ZnCl_4$		5
$[Co(ibn)(dpt)Cl]ZnCl_4$		3
$[Co(2,3\text{-tri})(en)Cl]ZnCl_4$		2
$[Co(trien)(NH_3)Cl]ZnCl_4$	1[8]; 3[20]; 3[21]	b
$[Co(dien)(NH_3)_2Cl]ZnCl_4$	2[20]	b

a Satisfactory analyses have been obtained for all of the isomeric forms listed in the table. Full details of the experimental methods are presented in Chapter 2.

b Not investigated here.

by analysis, infrared spectra, visible absorption spectra and X-ray powder diffraction patterns, and these will be described in detail in Chapter 2, along with the preparation of the μ-peroxo complexes.

INTRODUCTION: TRANS-TRIACIDO (TRIAMINE) COBALT III COMPLEXES

Cobalt (III) complexes of triamines most often contain the ligand coordinated to three of the six coordination positions on the cobalt. Previously, the complexes trans-$Co(dien)X_3$[23,55-59] and ? - $Co(dpt)X_3$[28,60] have been prepared and characterised. Attempts to prepare cis - $Co(dien)X_3$ have been unsuccessful[57].

In order to confirm the configuration of the $Co(dpt)X_3$ complexes, a series of complexes of the type $Co(dien)X_3$, $Co(2,3\text{-tri})X_3$ and $Co(dpt)X_3$ were prepared and their visible absorption and reflectance spectra were studied.

In addition, related complexes of the ligand 4-dodecyldiethylenetriamine, 4-dodec-dien, were studied.

Trans - Triacido(triamine)cobalt (III) Complexes with Tridentate Polyamine Ligands[61]

In an investigation to determine the extent to which increase in ring size influences the stereochemistry of facultative ligands, the following Cobalt (III) complexes were prepared; $Co(dien)X_3$, $Co(2,3\text{-tri})X_3$ and $Co(dpt)X_3$ ($X = NO_2^-$, Cl^-, Br^-, N_3^-, NCS^-). In this system the chelate ring systems are extended from two 5-membered rings, through one 5 and 6 membered ring, to two 6-membered rings,

and for the chloro complexes, the colours are brown, brown and green, respectively.

These complexes can theoretically exist in both facial (cis) and peripheral (trans) configurations, and in addition, both forms of $Co(2,3\text{-tri})X_3$ are potentially optically active by virtue of the asymmetric coordinated secondary amine group (Fig. 1.1).

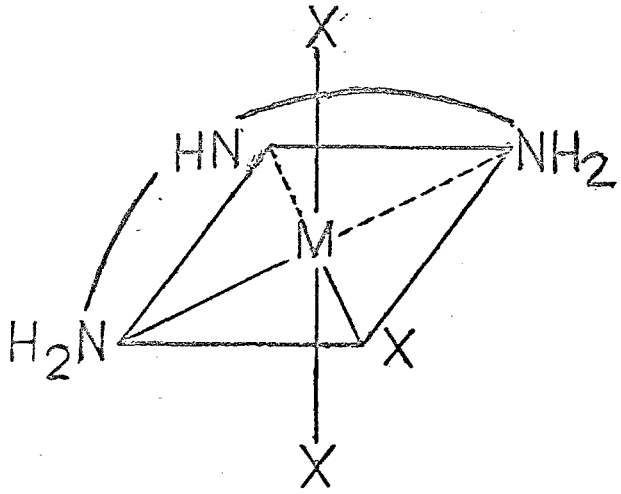
EXPERIMENTAL

Preparation of Complexes

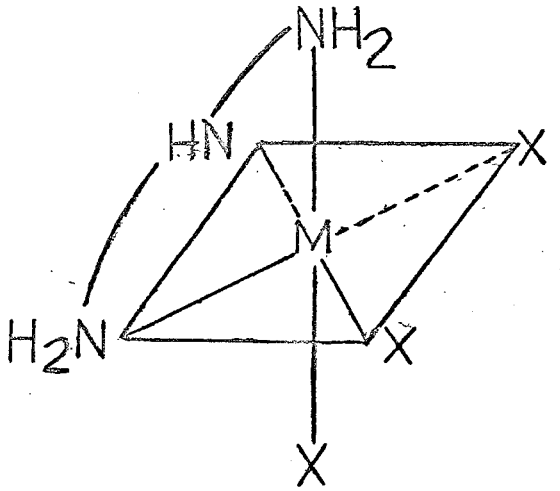
$Co(dpt)(NO_2)_3$[28,60], $Co(dien)(NO_2)_3$[22,57], $Co(dpt)Cl_3$[28,60], $Co(dien)Br_3$[58] and $Co(dien)Cl_3$[57,59] were prepared by the literature methods using the commercial amines. 2,3-tri was obtained from Ames Laboratories and used without further purification. Analytical data for the previously described compounds were in satisfactory agreement with the formula, and data for the previously unreported complexes are presented in Table 1.2.

$Co(2,3\text{-tri})X_3$ Complexes

$Co(2,3\text{-tri})(NO_2)_3$ was prepared from $CoCl_2.6H_2O$, $NaNO_2$ and 2,3-tri, using the method of Bosnich and Dwyer[22] for the preparation of $Co(dien)(NO_2)_3$. An 89 per cent yield of the yellow complex was obtained. A sample for analysis was recrystallised from dilute acetic acid. $Co(2,3\text{-tri})Cl_3$ was prepared by heating the trinitro complex in 12 F HCl for 30



Trans



Cis

Figure 1.1. Possible Geometric Isomers of $Co(ABA)X_3$, ABA = linear tridentate polyamine.

Table 1.2

Analytical Data

Complex	Formula	Calculated				Found			
		C%	H%	N%	Co%	C%	H%	N%	Co%
Co(dien)Br_3	$CoC_4H_{13}N_3Br_3$	11.95	3.26	10.46	14.66	12.54	3.30	10.38	14.83
Co(dien)$(N_3)_3$	$CoC_4H_{13}N_{12}$	16.67	4.55	58.33	20.45	17.02	4.60	58.76	20.28
Co(dien)$(NCS)_3$	$CoS_3C_7H_{13}N_6$	25.00	3.89	24.99	17.52	25.07	3.93	24.91	17.59
Co(2,3-tri)Cl_3	$CoC_5H_{15}N_3Cl_3$	21.26	5.35	14.87	20.86	21.80	5.30	14.27	20.89
Co(2,3-tri)Br_3	$CoC_5H_{15}N_3Br_3$	14.44	3.64	10.10	14.17	14.68	3.79	9.84	14.19
Co(2,3-tri)$(N_3)_3$	$CoC_5H_{15}N_{12}$	19.87	5.00	55.62	19.50	19.55	4.80	55.39	19.45
Co(2,3-tri)$(NCS)_3$	$CoS_3C_8H_{15}N_6$	27.43	4.32	23.99	16.82	27.57	4.21	23.81	16.93
Co(2,3-tri)$(NO_2)_3$	$CoC_5H_{15}N_6O_6$	19.12	4.81	26.75	18.76	19.62	5.11	26.08	18.07
Co(dpt)Br_3	$CoC_6H_{17}N_3Br_3$	16.76	3.99	9.77	13.71	17.01	4.21	10.57	13.68

minutes. Brown crystals deposited from the cool solution in a 78 per cent yield. These were washed successively with water, 2-propanol and ether.

Triazido Complexes

These were prepared from the trichloro complexes using the method of Curtis, Hay and Curtis[60], who prepared $Co(dpt)(N_3)_3$. $Co(dien)(N_3)_3$ and $Co(2,3\text{-tri})(N_3)_3$ are olive green. The yields were 83 per cent and 90 per cent respectively.

Tribromo Complexes

$Co(2,3\text{-tri})Br_3$ and $Co(dpt)Br_3$ were prepared from the trichloride complexes by heating them in water and then adding excess 63% HBr solution. The orange-brown salts that deposited were washed with water, 2-propanol and then ether. The yields were 55 per cent and 77 per cent respectively.

Triisothiocyanato Complexes

These were prepared by the method of Curtis, Hay and Curtis[60], who prepared $Co(dpt)(NCS)_3$. $Co(dien)(NCS)_3$ and $Co(2,3\text{-tri})(NCS)_3$ are red-brown. The yields were 62 per cent and 72 per cent, respectively.

RESULTS AND DISCUSSION

Of the fifteen triacidopolyamine cobalt (III) complexes described here, nine are new compounds and five of these contain the previously unreported ligand 1,4,8-triazaoctane, N-(2-aminoethyl)-1,3-diaminopropane, 2,3-tri. In this series, the yellow $Co(dien)(NO_2)_3$ has been shown by X-ray crystallography[62] to have the trans trinitro configuration, and there is substantial evidence that brown $Co(dien)Cl_3$ also has the trans trichloro arrangement[59,63].

Only the trinitro complexes have any stability in aqueous solution and the other compounds appear to follow $Co(dien)Cl_3$ which hydrolyses to various chloroaquo products in aqueous acidic solution[59]. DMF acts as a solvent for both the trinitro and triazido complexes but solvolysis of the latter may also be extensive as there are considerable differences between the visible reflectance and DMF solution spectra (Table 1.4).

On the basis of a colour comparison, it could be thought that the green $Co(dpt)Cl_3$ may have the cis trichloro configuration, especially as cis-$Cr(dien)Cl_3$ is also green.[58, 59,63,64] However, the reflectance spectra (Fig. 1.2, Table 1.3) of the trichloro complexes are all very similar, with only a progressive shift to longer wavelengths from dien to dpt, and a similar trans configuration is suggested. The

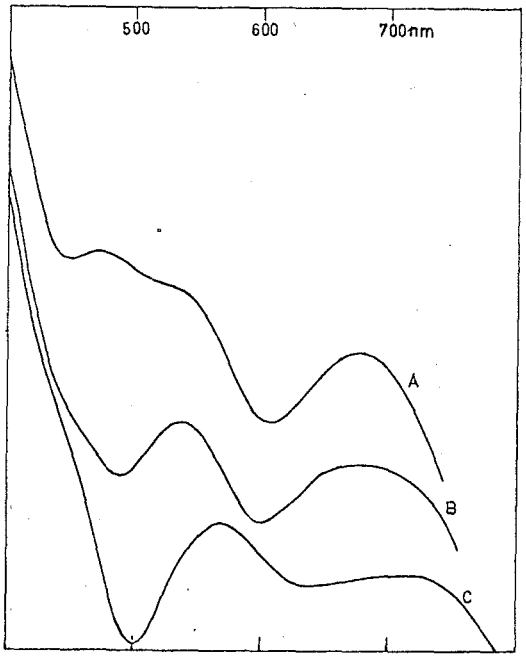


Figure 1.2 Solid state reflectance spectra of (A) $Co(dien)Cl_3$, (B) $Co(2,3\text{-tri})Cl_3$ and (C) $Co(dpt)Cl_3$. Wavelengths are in nanometers with an arbitrary intensity scale.

Table 1.3

Visible reflectance spectra[a] of $Co(dien)X_3$, $Co(2,3\text{-tri})X_3$ and $Co(dpt)X_3$ ($X = Cl^-, Br^-, NCS^-$)

$Co(dien)Cl_3$	$Co(2,3\text{-tri})Cl_3$	$Co(dpt)Cl_3$
675 max (670 max)[b]	680 max	720 max (736 max)[c]
605 min (610 min)[b]	600 min	635 min
535 sh (530 sh)[b]	535 max	568 max (572 max)[c]
	490 min	500 min
470 max (470 max)[b]	460 sh	450 sh (435 sh)[c]
447 min (450 min)[b]		
$Co(dien)Br_3$	$Co(2,3\text{-tri})Br_3$	$Co(dpt)Br_3$
720 max (740 max)[b]	710 max	710 max
652 min (650 min)[b]	635 min	650 min
510 max (510 max)[b]	475 max	470 sh
450 min (455 min)[b]	460 min	
$Co(dien)(NCS)_3$	$Co(2,3\text{-tri})(NCS)_3$	$Co(dpt)(NCS)_3$
512 max	517 max	538 max (546 max)[c]
470 min	465 min	488 min (467 min)[c]
333 max	338 max	334 max
260 sh	253 sh	280 sh

[a] Wavelengths in nanometers ± 5 nm: sh = shoulder.

[b] Data in parenthesis from Ref. 58.

[c] Data in parenthesis from Ref. 60.

red and brown tribromo and triisothiocyanato complexes exhibit similar changes in their reflectance spectra and the yellow trinitro and olive-green triazido complexes also have similar reflectance and solution spectra (Table 1.4).

It thus appears that this series of polyamine complexes adopts a trans configuration for the acido ligands Cl^-, Br^-, No_2^-, N_3^- and NCS^- regardless of the size of the rings formed by the polyamine. Previous observations on this effect have shown that in the tetraamine series, increase in ring size of the polyamine ligand enhances the stability of trans diacido complexes[65].

In this series of complexes, only $Co(ABA)(OH_2)_3^{3+}$ (ABA = dien[59], 2,3-tri[59a]) have been reported with cis configurations.

Complexes of 4-dodec-dien

$Co(4\text{-dodec-dien})(NO_2)_3$: $Na_3Co(NO_2)_6$ (8 g) was dissolved in water (25 ml) at 40° and 4-dodecyl-diethylene triamine (2 g) dissolved in ethanol (15 ml) was added. The orange-yellow product was immediately deposited and it was collected, washed with acetone and then ether. The yield was 77%.

$Co(4\text{-dodec-dien})Cl_3$: $Co(4\text{-dodec-dien})(NO_2)_3$ (1 g) was suspended in 12 F HCl (5 ml) and the solution was heated at 60° for 20 min. The resultant pale purple solid was collected, washed with 2-propanol and then ether. The yield was 88%.

Table 1.4

Absorption Maxima in the visible and u.v. spectra of $Co(dien)X_3$, $Co(2,3\text{-tri})X_3$ and $Co(dpt)X_3$ ($X = NO_2^-$, N_3^-).

Complex	Refl.[a,b]	DMF[a,c]	H_2O[d]	H_2O[e]
$Co(dien)(NO_2)_3$	240		250	250
	330	345	338	330
	435sh	435sh	433	435
$Co(2,3\text{-tri})(NO_2)_3$	240			
	330	346		
	442	438		
			MeOH[f]	
$Co(dpt)(NO_2)_3$	244			
	333	348		
	454, 466[f]	453	452	
	Refl.[a,b,g]			
$Co(dien)(N_3)_3$		337		
	510sh			
	610	575		
$Co(2,3\text{-tri})(N_3)_3$		340		
		550sh		
	595br	590		
$Co(dpt)(N_3)_3$		348		
	595, 595[f]	612		
	710, 724[f]			

a This work; wavelengths in nanometers ±5nm; sh = shoulder; br = broad. b Refl. = reflectance spectra. c 320-800 nm range. d Data from Ref. 57. e Data from Ref. 66. f Data from Ref. 60. g 400-800 nm range.

Table 1.5

Analytical Data

Complex	Formula	Calculated			Found		
		C%	H%	Co%	C%	H%	Co%
Co(4-dodec-dien)Cl_3	$CoC_{16}H_{37}N_3Cl_3$	44.00	8.54	13.49	44.10	8.71	13.57
Co(4-dodec-dien)Br_3	$CoC_{16}H_{37}N_3Br_3$	33.71	6.54	10.34	33.92	6.61	10.39
Co(4-dodec-dien)$(N_3)_3$	$CoC_{16}H_{37}N_{12}$	42.11	8.15	12.91	42.31	8.03	12.72
Co(4-dodec-dien)$(NO_2)_3$	$CoC_{16}H_{37}N_6O_6$	41.02	7.96	12.58	40.75	7.92	12.41

Table 1.6

Visible reflectance spectra[a] of $Co(4\text{-dodec-dien})X_3$.

$Co(4\text{-dodec-dien})Cl_3$	$Co(4\text{-dodec-dien})Br_3$
674 max	694 max
643 min	630 min
630 max	
603 min	
540 max	494 max
455 min	460 min
317 max	314 max
270 sh	270 sh
$Co(4\text{-dodec-dien})(N_3)_3$	$Co(4\text{-dodec-dien})(NO_2)_3$
575 max	625 sh
505 min	430 sh
335 max	332 max
270 sh	268 min

[a] Wavelengths in nanometers ± 5 nm: sh = shoulder

Co(4-dodec-dien)Br_3: Co(4-dodec-dien)$(NO_2)_3$ (0.2 g) was suspended in water (15 ml) and 63% HBr (10 ml) was added. The solution was heated at 60° for 15 min. and the resultant brown solid was collected, washed with acetone and then ether. The yield was 95%. The product oils if washed with 2-propanol.

Co(4-dodec-dien)$(N_3)_3$: Co(4-dodec-dien)Cl_3 was suspended in 0.2 F CH_3CO_2H (15 ml) and NaN_3(4 g) was added. The solution was heated on a steam bath (ca. 80°) for 1 hr. The resultant green solid was collected, washed with acetone and then ether. The yield was 91%. The product is sparingly soluble in 2-propanol.

Analytical data are presented in Table 1.5. The reflectance spectra of the complexes (Table 1.6) are very similar to those of Co(dien)X_3 (Table 1.3 and 1.4) and these indicate that the triamine adopts a trans configuration in these complexes. From this limited data, it appears that large substituents on the triamine have no influence in determining the stereochemistry of the coordinated tridentate polyamine.

C H A P T E R 2

OCTAHEDRAL COMPLEXES OF THE ACIDOPENTAAMINECOBALT (III) TYPE

EXPERIMENTAL SECTION

EXPERIMENTAL SECTION

The commercial amines were used without further purification. Meso-Stilbenedlamine was kindly prepared by Mr W.A. Sadler using the method of Irving and Parkins[69]. All other chemicals were of reagent grade quality. $[Co_2(en)_2(dien)_2O_2](ClO_4)_4.2H_2O$[67] $Na_3[Co(CO_3)_3].3H_2O$[68], trans-$Co(dien)(NO_2)_3$[23], trans-$Co(dien)Cl_3$[57-59], green cis-$Cr(dien)Cl_3$[59,64], trans-$Co(2,3\text{-tri})(NO_2)_3$[61], trans-$Co(dpt)(NO_2)_3$[28] and trans-$Co(dpt)Cl_3$[60] were prepared by the literature methods, or by methods described in this work. Infrared spectra of the tetrachlorozincate (II) salts were used to determine the isomeric composition of the chloro complexes. Each of the infrared distinguishable isomers (or co-crystallising chloro-nitro mixtures that do not change composition on recrystallisation)have been assigned an alphabetical letter, Greek letter or roman numeral in an arbitrary but systematic manner. The chloro-nitro mixtures are distinguished by inverted commas, e.g. "ε". In most cases the syntheses involving fractional crystallisation have been duplicated with essentially similar results for the isomeric composition of the collected fractions.

(A) Complexes of 1,2-diamines with diethylenetriamine

(1) Ethylenediamine[72]

Analytical data for the complexes are presented in Tables 2.2 and 2.3. Infrared spectra of the chloro $ZnCl_4^{2-}$ salts in the region 1700-400 cm^{-1} (KBr Disc) are presented in Fig. 2.1.

Isomers of Chloro(ethylenediamine)(diethylenetriamine)cobalt (III) Tetrachlorozincate (II);

Method A: $[Co_2(en)_2(dien)_2O_2](ClO_4)_4.2H_2O$ (30 g) was added to a solution of 12 F HCl (85 ml) in water (170 ml) containing $ZnCl_2$ (50 g). The solution was heated on a steam bath (ca. 80°) until the effervescence ceased (30 min) during which time a red crystalline material was deposited. The solution was cooled to room temperature and the product was collected, washed with 2-propanol and then ether; yield 13 g. The crude product was recrystallised by dissolving it in the minimum volume of 0.2 F HCl at 50° (ca. 150 ml) and then adding 12 F HCl (50 ml) containing $ZnCl_2$ (25 g). The product that deposited was collected from the cooled solution and it was washed and dried as above. Losses were mechanical and the product was a π-K mixture in a 42% yield.

The original mother liquor (orange-brown) was again heated at 80° and after 30 min. a further 50 ml portion of 12 F HCl was added to the solution. An orange-red product

slowly deposited and this was collected and washed as above. The product was recrystallised as above but using a corresponding reduction in volumes and weights of the reagents used. The yield was 1.5 g of the pure *K* isomer. The total yield of chloropentaamine complex was 47%.

Method B: Trans-$Co(dien)(NO_2)_3$ (15 g) was suspended in water (30 ml) and ethylenediamine (3.3 ml, 100%) was added. The solution was stirred and allowed to digest the neutral complex on a steam bath for one hour. The filtered solution was heated to 80° and 12 F HCl (30 ml) was cautiously added. Heating was continued for a further hour, during which time the evolution of nitrogen oxides subsided, and a deep red colour was produced. $ZnCl_2$ (15 g) and 12 F HCl (5 ml) were then added and after heating for a further 30 min., the product commenced to crystallise. The product was collected in about 2 g fractions, which were washed with 2-Propanol and then ether. Each fraction was recrystallised by dissolving the crude complex in the minimum volume of 0.2 F HCl at 25° (1 g/50 ml) and then adding 12 F HCl (25 ml/1 g) containing $ZnCl_2$ (5 g/1 g). The products were again collected in fractions and were collected, washed and dried as above. The total yield was 7.7 g or 36% and fractions after the fourth crop were increasingly contaminated with orange-yellow impurities, possibly hexaamine salts. The isomeric composition of the fractions are tabulated in Table

Table 2.1

Isomeric Composition of fractions of $[Co(en)(dien)Cl]ZnCl_4$; Method B

Crop 1			Crop 2		Crop 3	
1	2	3	1	2	1	2
1.1**	0.7	0.5	1.6	0.7	0.6	0.5
(ε)	(ε)	(ε)	(ε)	(ε)	(ω)	(ω+ε)

Crop 4			
1	2	3	4
0.6	0.7	0.4	0.3
(ε+κ)	(ε+κ+ω)	(ε+κ)	(ε+κ)

** weight in g.

2.1.

Method C: The method of Bosnich and Dwyer[23,24] was followed on a 1/20 scale. The crude product was converted to the tetrachlorozincate (II) salt by dissolving it in the minimum volume of 50° 0.1 F HCl and then adding excess 12 F HCl containing $ZnCl_2$. The material that deposited on cooling the solution in an ice bath was collected in fractions, washed with 2-propanol and then ether (Crops 1-4). The original mother liquor was heated to 50° and 12 F HCl (20 ml) containing $ZnCl_2$ (10 g) was added. The product that deposited was collected in fractions and recrystallised as above (Crops 5-7). The total yield was 12.4 g or 63%. The 1st, 2nd and 3rd crops were the pure ω isomer (6.5 g), the 4th crop an "ε"-ω mixture, the 5th and 6th crops a π-*K* mixture and the 7th crop consisted of the *K* isomer contaminated with orange impurities, possibly hexaamine salts.

Method D: $CoCl_2.6H_2O$ (7 g), NH_4Cl (25 g) and NH_4I (0.5 g) were added to 40 ml of water and I_2 (3.7 g) dissolved in 80 ml of ethanol was added to the stirred aqueous suspension. This was followed by the addition of ethylenediamine (2.1 ml, 100%) and diethylenetriamine (3,4 ml, 100%) in water (20 ml). The mixture was stirred at room temperature for three hours, during which time a deep red colour developed. The solution was allowed to stand overnight when red needle-like crystals along with some NH_4Cl were deposited.

The crude product was converted to the $ZnCl_4^{2-}$ salt as in Method C. Two further crops were obtained by addition of acetone and methanol (150 ml of a 1:1 mixture) after filtration of the precipitated ammonium salts and these were converted to the $ZnCl_2^{2-}$ salt. A total yield of 0.8 g of the pure ω isomer was obtained. Finally, the mother liquor (450 ml) was evaporated on a steam bath to 250 ml and 12 F HCl (50 ml) containing $ZnCl_2$ (15 g) was added. The red product that deposited from the ice cooled solution was collected in 1-2 g fractions. These were washed with 2-propanol and ether and recrystallised as before. The three crops that were collected consisted of a π-*K* mixture and the third crop also contained some ω isomer. The total yield was 6 g or 45%.

Method E: Freshly prepared $Na_3[Co(CO_3)_3].3H_2O$ (10 g) was suspended in water (30 ml) and a mixture of ethylenediamine (2.15 ml, 100%) and diethylenetriamine (4.95 ml, 100%) was added. After heating at 80° for 15 min., 12 F HCl (20 ml) containing $ZnCl_2$ (10 g) was cautiously added to the now red solution. Successive crystal crops were collected over a period of several days and these were recrystallised as in Method A. Crop one and two (0.5 g) each consisted of the π isomer and the third crop was a π-ω-*K* mixture (0.6 g). Subsequent crops were contaminated with hexaamine salts. The yield of the chloropentaamine complex was only 9%.

Separation of a π-*K* Mixture

Method 1: The mixture of the π-*K* isomers (generated by Method A, ca. 35% *K* isomer) was dissolved in 0.2 F $HClO_4$ (15 g, 150 ml) and twice the weight of solid $NaClO_4.H_2O$ was stirred in. Pure *K*-[Co(en)(dien)Cl]$(ClO_4)_2$ (5 g) was deposited immediately and this was collected, washed with 2-propanol and then ether. 12 F HCl (50 ml) containing $ZnCl_2$ (20 g) was added to the mother liquor and the pure or partly purified π-[Co(en)(dien)Cl]$ZnCl_4$ was precipitated. This was recrystallised as described previously in Method A. *K*-[Co(en)(dien)Cl]$ZnCl_4$ was made from the perchlorate salt by dissolving the latter in water (5 g/50 ml) and then adding 12 F HCl (25 ml) containing $ZnCl_2$ (10 g) . The precipitated product was collected, washed and dried as above. Losses in this procedure were mechanical.

Method 2: The π-*K* isomeric mixture (20 g) generated by Method A, was dissolved in water (150 ml) and a solution of KOH (20 g) in water (50 ml) was added. The solution was heated at 60° for 20 min., filtered, cooled in ice, and ice cold 12 F HCl (350 ml) containing $ZnCl_2$ (20 g) was added dropwise. The orange coloured solution was set aside at room temperature and after 2 days, the first crystal crop (3 g of pure π-[Co(en)(dien)Cl]$ZnCl_4$) was collected, washed with 2-propanol, then ether and finally air dried. Subsequent crops were again π-*K* mixtures (14 g).

Qualitative Isomerisation Reactions

Small quantities of the pure isomers were taken and subjected to the following chemical reactions. The isomeric composition of the chloro $ZnCl_4^{2-}$ product was determined by examination of the infrared spectrum.

(a) Base Hydrolysis. The π, "ε", ω and *K* isomers of $[Co(en)(dien)Cl]ZnCl_4$ were separately dissolved in water (0.25 g/15 ml, 0.25 g/15 ml, 0.1 g/15 ml and 0.25 g/15 ml respectively) and ca. 10 ml of 1 F NaOH was added until all the $Zn(OH)_2$ had precipitated. The solutions were heated at 70° for 20 min. and then 12 F HCl (10 ml) containing $ZnCl_2$ (4 g) was added. The solutions were left to stand at room temperature overnight and the product was collected, washed with 2-propanol and then ether. The results were:
ω → π + *K*; "ε" → π; *K* → π + *K*; π → π.

(b) Reflux in 6 F HCl. The pure isomers of $[Co(en)(dien)Cl]ZnCl_4$ were separately dissolved in 6 F HCl (0.2 g/25 ml) and the solutions were boiled under reflux for 1 hour. 12 F HCl (15 ml) containing $ZnCl_2$ (5 g) was then added and the products that deposited from the ice cooled solutions were collected, washed with 2-propanol and then ether. The results were: *K* → *K*; π → π; ω → ω; "ε" → π.

(c) Reflux in 0.05 F HCl. Similar amounts and conditions were used as in (b) except that the 6 F HCl was replaced by 0.05 F HCl. The results were: "ε" → π + *K* + "ε"; *K* → *K* + π; π → π + *K*; ω → ω.

(d) Reaction with Nitrous Acid. Nitro compounds derived from the π, *K*, "ε" and ω-[Co(en)(dien)Cl]$ZnCl_4$ isomers were prepared using the method described later in this section. These were decomposed by heating (ca. 80°) a solution of each in 3 F HCl for 1 hour. The $ZnCl_4^{2-}$ salts of the chloro isomers generated in this manner were deposited by the addition of $ZnCl_2$. The transformations that resulted were: π → "ε"; *K* → *K*; "ε" → "ε"; ω → ω.

Perchlorate Salts. The isomerically pure [Co(en)(dien)Cl] $ZnCl_4$ salts (0.5 g) were separately dissolved in the minimum volume of 80° 3 F $HClO_4$ (25-30 ml) and excess $NaClO_4.H_2O$ (ca. 5 g) was added. The products that crystallised from the ice cooled solutions were collected, washed with 2-propanol, then ether and air dried. The "ε" and π isomers crystallised as the diperchlorate monohydrates, the *K* isomer as the diperchlorate and the ω isomer as the chloride-perchlorate salt.

Table 2.2

Analytical Data for [Co(en)(dien)Cl]X.

Complex	Calculated					Found				
	C%	H%	N%	Co%	X%[a]	C%	H%	N%	Co%	X%[a]
[Co(en)(dien)Cl]$ZnCl_4$ - ω	15.5	4.55	15.0	12.7	38.2	15.9	4.56	14.9	12.6	37.8
- π						15.8	4.64	15.1	12.6	38.1
- κ						15.7	4.59	14.9	12.6	38.1
[Co(en)(dien)Cl]$(ClO_4)_2$ - κ	15.78	4.64	15.34	12.91	7.77	15.75	4.72	14.96	12.85	7.71
[Co(en)(dien)Cl]$(ClO_4)_2.H_2O$ - π	15.18	4.88	14.75	12.41	7.47	15.09	4.96	15.08	12.44	7.85
[Co(en)(dien)Cl]$Cl(ClO_4)$ - ω	18.35	5.39	17.84	15.01	18.06	18.46	5.51	17.61	15.50	18.25

a Total Halide as found by Ag^+ titration.

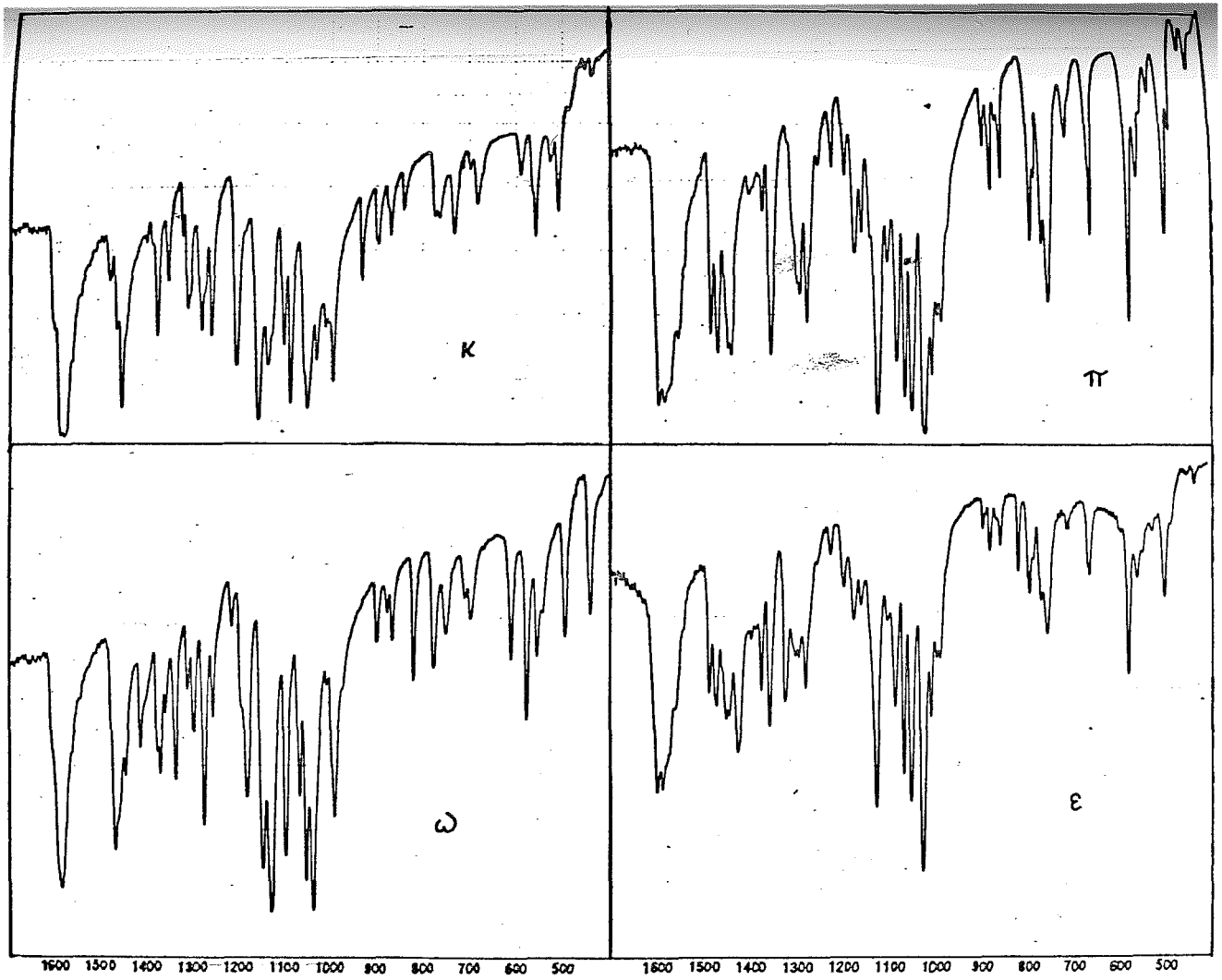


Figure 2.1 Infrared spectra of π, " ε", ω , and κ -[Co(en)(dien)Cl]$ZnCl_4$ in the range 1700-400 cm^{-1} (KBr Disc).

ω, *K* and π-Chloro(ethylenediamine)(diethylenetriamine)cobalt (III) Tetrabromozincate (II): The ω, *K* and π isomers of $[Co(en)(dien)Cl]ZnCl_4$ (0.20 g, 0.25 g, 0.5 g respectively) were separately dissolved in dilute acid (25 ml 0.2 F CH_3CO_2H, 15 ml 0.1 F HCl, 15 ml 0.1 F HCl) and 63% HBr (5 ml, 10 ml, 10 ml) containing $ZnBr_2$ (1 g, 2 g, 2 g) was added. The products, that deposited on cooling to room temperature, were collected from the well cooled solutions, washed with 2-propanol and then ether. The yields were ω 66%, *K* 81%, π 58%.

ω, *K* and π-Chloro(ethylenediamine)(diethylenetriamine)cobalt (III) Tetrathiocyanato zincate (II): The ω, *K* and π isomers of $[Co(en)(dien)Cl]ZnCl_4$ were separately dissolved in 0.2 F CH_3CO_2H at 80° (0.20 g/30 ml, 0.25 g/25 ml, 0.5 g/50 ml, respectively) and a solution of NH_4NCS (1 g, 1 g, 2 g) in water (5 ml, 5 ml, 10 ml) was added. The tetrathiocyanato-zincate (II) salts were deposited slowly on cooling to room temperature. The products were collected from the well cooled solutions, washed with two 5 ml portions of ice water, 95% ethanol (2-propanol for the ω product) and air dried. The yields were ω 95%, *K* 90% and π 94%.

The ω product forms an oil if washed with 95% ethanol.

π-Chloro(ethylenediamine)(diethylenetriamine)cobalt(III) Tetrachlorocobaltate(II): π-[Co(en)(dien)Cl]$ZnCl_4$ (0.5 g) was dissolved in 1 F HCl (5 ml) and $CoCl_2.6H_2O$ (3 g) dissolved in 12 F HCl (10 ml) was added. After cooling at 0-5° for three days, the dark blue crystalline product that was slowly deposited was collected, washed with 2-propanol and then ether. The yield was 26.5%.

π-Chloro(ethylenediamine)(diethylenetriamine)cobalt(III) Tetraiodozincate(II): π-[Co(en)(dien)Cl]$ZnCl_4$ (0.5 g) was dissolved in 0.2 F CH_3CO_2H (50 ml) and $Zn(ClO_4)_2$ (1 g) and NaI (5 g) were added. The product that was deposited immediately was collected, washed with 2-propanol and then ether.

The crude product was recrystallised by dissolving it in 0.2 F CH_3CO_2H (50 ml) and then adding a solution of $Zn(ClO_4)$, (1 g) and NaI (5 g). The product that was deposited was collected, washed and dried as above. The yield was 68%.

This complex is unstable, changing in one month to a green powder from which the ω-Co(en)(dien)I^{2+} cation can be extracted in high yield.

ω and *K*-Chloro(ethylenediamine)(diethylenetriamine)cobalt(III) Iodide: The ω and *K* isomers of $[Co(en)(dien)Cl]ZnCl_4$ were separately dissolved in 0.2 F CH_3CO_2H at 50° (0.2 g/20 ml) and NaI (4 g) was added. On standing in an ice-bath for 2 hours, the crystalline products that were slowly deposited were washed with 2-propanol and then ether. The yields were ω 74%, *K* 66%.

ω-Bromo(ethylenediamine)(diethylenetriamine)cobalt(III) Bromide Monohydrate and ω-bromo(ethylenediamine)(diethylenetriamine)cobalt(III) Tetrabromozincate(II): A solution of ω-$[Co(en)(dien)Cl]ZnCl_4$ (0.5 g) in water (10 ml) containing 63% HBr (2 ml) was refluxed for 30 min. The resultant red-violet solution was cooled to 40° and the pale violet crystals of the bromide salt that were deposited were collected, washed with acetone and then ether. The yield was 48%.

A solution of 63% HBr (5 ml) containing $ZnBr_2$ (2 g) was then added to the mother liquor and the crystalline tetrabromozincate(II) salt that deposited was collected, washed with 2-propanol one then ether. The yield was 29%.

K and π-Bromo(ethylenediamine)(diethylenetriamine)cobalt(III) Tetrabromozincate(II):

Method A: $[Co_2(en)_2(dien)_2O_2](ClO_4)_4 \cdot 2H_2O$ (3 g) was added to a solution of 20% HBr (30 ml) containing $ZnBr_2$ (5 g).

The solution was heated on a steam bath (ca. 80°) and after 15 min. the crude product commenced to crystallise. The heating was continued for a further 20 min. and then the solution was allowed to cool to room temperature. The product was collected in fractions at 15° intervals, washed with 2-propanol and then ether.

The crude product was recrystallised by dissolving it in 0.2 F CH_3CO_2H (0.1 g/20 ml) and then adding 63% HBr (5 ml/0.1 g) containing $ZnBr_2$ (2 g/0.1 g). The purified product was collected, washed and dried as above. The yield was 42%. The isomeric composition of the fractions was:

Fraction No.	Weight (g)	Isomeric Composition	Approximate Temperature (°C)
1	0.40	*K*	75
2	1.37	*K*	60
3	0.78	*K* + π	45
4	1.25	π	30

Method B: A solution of *K*-$[Co(en)(dien)Cl](ClO_4)_2$ (0.85 g) in water (15 ml) containing 63% HBr (3.5 ml) was boiled under reflux for 30 min. The solution was then cooled to 30° and HBr (10 ml) containing $ZnBr_2$ (2.5 g) was added. The purple product that was immediately deposited was collected, washed with 2-propanol and then ether. The crude product was recrystallised by dissolving it in 0.2 F CH_2CO_2H (0.1 g/6 ml) at 60° and then adding 63% HBr (2 ml/0.1 g)

containing $ZnBr_2$ (2 g/0.1 g). The product that deposited on cooling was collected in fractions, washed and dried as above. The yield was *K* 58%. The final fraction contained 50% of the π isomer.

The reaction using π-$[Co(en)(dien)Cl]ZnCl_4$ as the starting material produces the *K* isomer as the major component in the product.

Method C: *K*-$[Co(en)(dien)Cl]ZnCl_4$ (1 g) was dissolved in water (25 ml) and Ag_2O (1.2 g) was added. The mixture was heated at 60° for 15 min. and it was then filtered. 63% HBr (15 ml) containing $ZnBr_2$ (3 g) was then added and the pale purple product was slowly deposited on cooling in an ice bath. After 24 hr at 0-5°, the product was collected, washed with 2-propanol and then ether. The yield was *K* 35%.

ω, *K* and π-Bromo(ethylenediamine)(diethylenetriamine)cobalt (III) Tetrachlorozincate(II): The *K* and π isomers of $[Co(en)(dien)Br]ZnBr_4$ (0.5 g, 0.2 g respectively) and ω-$[Co(en)(dien)Br]Br_2.H_2O$ (0.1 g) were separately dissolved in 0.2 F CH_3CO_2H (30 ml, 12 ml, 10 ml respectively) at 40° and a solution of 12 F HCl (10 ml, 4 ml, 4 ml) containing $ZnCl_2$(2.5 g, 1 g, 1 g) was added. The purple products were deposited immediately and they were collected from the well cooled solutions, washed with 2-propanol and then ether. The yields were ω 85%, *K* 90% and π 87%.

ω, *K* and π-Bromo(ethylenediamine)(diethylenetriamine)cobalt (III) Tetrathiocyanatozincate(II): The *K*, π and ω isomers of $[Co(en)(dien)Br]ZnBr_4$ were separately dissolved in 0.2 F CH_3CO_2H (0.06 g/10 ml, 0.25 g/25 ml, 0.15 g/15 ml respectively) at 50° and a solution of NH_4NCS (0.5 g, 1.5 g, 1.5 g) in water (2 ml, 10 ml, 5 ml) was added. The purple products were collected, washed with ice water, 2-propanol and were then air dried. The yields were ω 83%, *K* 85% and π 88%.

K-Bromo(ethylenediamine)(diethylenetriamine)cobalt(III) Tetrachlorocadmiumate(II): *K*-$[Co(en)(dien)Br]ZnBr_4$ (0.20 g) was dissolved in water (5 ml) and a solution of 12 F HCl (5 ml) containing $CdCl_2$ (2 g) was added. The purple product, that was immediately deposited, was collected from the well cooled solution, washed with 2-propanol and then ether. The yield was 25.2%.

K-Bromo(ethylenediamine)(diethylenetriamine)cobalt(III) Tetrabromocadmiumate(II): *K*-$[Co(en)(dien)Br]ZnBr_4$ (0.2 g) was dissolved in 0.2 F CH_3CO_2H (15 ml) and a solution of 30% HBr (10 ml) containing $CdBr_2.4H_2O$ (6 g) was added. The purple product that deposited on cooling to room temperature was collected, washed with 2-propanol and then ether. The yield was 91.9%.

K and π-Bromo(ethylenediamine)(diethylenetriamine)cobalt(III) Perchlorate: The *K* and π isomers of $[Co(en)(dien)Br]ZnBr_4$ (0.5 g) were separately dissolved in 3 F $HClO_4$ (10 ml) at 60° and $NaClO_4.H_2O$ (6 g) was added. The crystalline products, that were slowly deposited on cooling the solution in an ice bath were collected, washed with 2-propanol and then ether. The yields were *K* 55.0% and π 21.9%.

ω and *K*-Iodo(ethylenediamine)(diethylenetriamine)cobalt(III) Iodide Monohydrate: Solutions of a π/*K* mixture of $[Co(en)(dien)Cl]ZnCl_4$ (2 g) and NaI (10 g) in water (40 ml) were (a) heated on a steam bath, and (b) refluxed, for 30 min. The olive green products that deposited on the addition of NaI (5 g) were collected, washed with acetone and then ether. The crude products were recrystallised by dissolving them in 0.2 F CH_3CO_2H (50 ml, 15 ml) at 50° and then adding NaI (10 g) dissolved in water (10 ml). The green products that were deposited on cooling were collected, washed and dried as above. The yields were: (a) *K* 25%, (b) ω 69%.

K-Iodo(ethylenediamine)(diethylenetriamine)cobalt(III) Tetrachlorozincate(II): *K*-$[Co(en)(dien)Cl]ZnCl_4$ (1 g) was dissolved in water (10 ml) and NaI (2 g) dissolved in water (5 ml) was added. The solution was heated on a steam bath (ca. 80°) for 30 min. The solution was cooled to 40° and then NaI (10 g) was added. The brown product was collected

and washed with acetone. The crude product was dissolved in 0.1 F HCl (25 ml) at 50° and a solution of 12 F HCl (15 ml) containing $ZnCl_2$ (5 g) was added. The product, that deposited on cooling in an ice bath was collected, washed with 2-propanol and then ether. The yield of the *K* isomer was 65%.

ω-Iodo(ethylenediamine)(diethylenetriamine)cobalt(III) Tetrachlorozincate (II): ω-$[Co(en)(dien)Cl]ZnCl_4$ (0.5 g) was dissolved in water (8 ml) and a solution of NaI (1 g) dissolved in water (1.5 ml) was added. The solution was refluxed for 30 min. and then NaI (5 g) was added to the resultant yellow-brown solution. After cooling in an ice bath, the brown product was collected and washed with acetone. The crude product was dissolved in 0.1 F HCl (0.1 g/5 ml) and a solution of 12 F HCl (10 ml) containing $ZnCl_2$ (2.5 g) was added. The green product that deposited slowly from the ice cooled solution was collected, washed with 2-propanol and then ether. The yield was 20%.

ω-Iodo(ethylenediamine)(diethylenetriamine)cobalt(III) Tetrabromozincate(II): ω-$[Co(en)(dien)I]I_2.H_2O$ (0.25 g) and $Zn(CH_3CO_2)_2$ (2 g) were dissolved in 0.2 F CH_3CO_2H (20 ml) at 50° and 63% HBr (10 ml) was added. The green product that was immediately deposited was collected from the ice cooled solution, washed with 2-propanol and then ether. The yield was 83%.

ω-Iodo(ethylenediamine)(diethylenetriamine)cobalt(III) Perchlorate: ω-$[Co(en)(dien)I]I_2$. H_2O (0.25 g) was dissolved in 1 F $HClO_4$ (15 ml) at 60°. The solution was filtered and the filtrate was added to $NaClO_4.H_2O$ (15 g). The brown product that deposited immediately was collected, washed with 2-propanol and then ether. The yield was 57%.

ω and *K*-Iodo(ethylenediamine)(diethylenetriamine)cobalt(III) Tetrathiocyanatozincate(II): The ω and *K* isomers of $[Co(en)(dien)I]ZnCl_4$ (0.03 g, 0.05 g respectively) were separately dissolved in 0.2 F CH_3CO_2H (5 ml, 10 ml) at 60° and a solution of NH_4NCS (0.5 g) in water (2 ml) was added. On cooling rapidly in an ice bath, the green products that were deposited were collected, washed with 2-propanol and then air dried. The yields were ω 80.2%, *K* 87.6%.

ω-Iodo(ethylenediamine)(diethylenetriamine)cobalt(III) Bromide Monohydrate: ω-$[Co(en)(dien)I]I_2.H_2O$ (0.2 g) was dissolved in water (30 ml) at 60° and 63% HBr (10 ml) was added. The dark green crystals that were deposited on cooling in an ice bath were collected, washed with acetone and then ether. The yield was 43.7%.

ω-Iodo(ethylenediamine)(diethylenetriamine)cobalt(III) Tetrachlorocadmiumate(II): ω-$[Co(en)(dien)\ I]I_2.H_2O$ (0.2 g) was dissolved in 0.2 F CH_3CO_2H (15 ml) and a solution of

6 F HCl (10 ml) containing $CdCl_2$ (2 g) was added. The product that deposited on cooling to room temperature was collected from the ice cooled solution, washed with 2-propanol and then ether. The yield was 64.8%.

ω-Iodo(ethylenediamine)(diethylenetriamine)cobalt(III) Tetrabromocadmiumate(II): ω-$[Co(en)(dien)I]ZnCl_4$ (0.2 g) was dissolved in 0.2 F CH_3CO_2H (15 ml) and a solution of 30% HBr (10 ml) containing $CdBr_2.4H_2O$ (6 g) at 80° was added. The green crystalline product that was immediately deposited was collected, washed with 2-propanol and then ether. The yield was quantitative.

K and π-Azido(ethylenediamine)(diethylenetriamine)cobalt(III) Tetrachlorozincate(II): The *K* and π isomers of $[Co(en)(dien)Cl]ZnCl_4$ (1 g) were separately dissolved in 0.2 F CH_3CO_2H (20 ml) and NaN_3 (3 g) was added. The solutions were heated on a steam bath (ca. 80°) for 20 min. and then were cooled to room temperature.

1:1 2-propanol/methanol (100 ml) containing 12 F HCl (1 ml) and $ZnCl_2$ (5 g) was added and the products that were slowly deposited on cooling in an ice bath, were collected, washed with 2-propanol and then ether. The yields were *K* 95%, π 72%.

ω-Azido(ethylenediamine)(diethylenetriamine)cobalt(III) Tetrabromozincate(II): ω-[Co(en)(dien)Cl]$ZnCl_4$ (0.5 g) was dissolved in 0.2 F CH_3CO_2H (10 ml) and NaN_3 (1.5 g) was added. The solution was boiled under reflux for 20 min. and then was cooled to 25°. A solution of 63% HBr (10 ml) containing $ZnBr_2$ (2 g) was then added and the purple-red product that was slowly deposited was collected in fractions, washed with 2-propanol and then ether. The initial fraction contains the *K* isomer. The yield of ω isomer was 55%.

K and π-Azido(ethylenediamine)(diethylenetriamine)cobalt(III) Tetrabromozincate(II): The *K* and π isomers of [Co(en)(dien)N_3]$ZnCl_4$ (0.50 g, 0.25 g respectively) were separately dissolved in water (25 ml, 10 ml) and a solution of 63% HBr (25 ml, 5 ml) containing $ZnBr_2$ (3 g, 2 g) was added. The dark red-purple crystalline products that were deposited on cooling in an ice bath were collected, washed with 2-propanol and then ether. The yields were *K* 85%, π 63%.

K and π-Azido(ethylenediamine)(diethylenetriamine)cobalt(III) Tetrathiocyanatozincate(II): The *K* and π isomers of [Co(en)(dien)N_3]$ZnCl_4$ (0.25 g) were separately dissolved in water (10 ml) and KNCS (1.5 g) was added. On standing at room temperature, the products, that were slowly deposited, were collected, washed with 2-propanol and then air dried. The yields were *K* 88%, π 85%

π-Azido(ethylenediamine)(diethylenetriamine)cobalt(III) Chloride Perchlorate: π-$[Co(en)(dien)N_3]ZnCl_4$ (0.5 g) was dissolved in 0.1 F $HClO_4$ (25 ml) at 50° and $NaClO_4.H_2O$ (10 g) was added. The purple-red crystalline product that was deposited on cooling in an ice bath was collected, washed with 2-propanol and then ether. The yield was 58%.

K-Azido(ethylenediamine)(diethylenetriamine)cobalt(III) Tetrabromocadmiumate(II): *K*-$[Co(en)(dien)N_3]ZnCl_4$ (0.15 g) was dissolved in 0.2 F CH_3CO_2H (10 ml) at 40° and a solution of 63% HBr (5 ml) containing $CdBr_2.4H_2O$ (2.5 g) was added. The product, that was immediately deposited, was collected from the ice cooled solution, washed with 2-propanol and then ether. The yield was 92.5%.

K and π-Nitro(ethylenediamine)(diethylenetriamine)cobalt(III) Tetrachlorozincate(II): The *K* and π isomers of $[Co(en)(dien)Cl]ZnCl_4$ (1 g) were separately dissolved in 0.2 F HCl (25 ml) and $NaNO_2$ (3 g) was added. The solutions were heated on a steam bath (ca. 80°) for one hour during which time the mild effervescence ceased and the colour changed from red to orange-yellow. The hot solution was slowly poured into 1:1 acetone/2-propanol (100 ml) containing 12 F HCl (1 ml) and $ZnCl_2$ (5 g). The yellow crystals that were deposited immediately were collected from the ice cooled solutions,

washed with acetone and then ether. The yields were *K* 84.3%, π 79.0%.

ω-Nitro(ethylenediamine)(diethylenetriamine)cobalt(III) Tetrachlorozincate(II): ω-$[Co(en)(dien)Cl]ZnCl_4$ (0.25 g) was dissolved in 0.2 F HCl (10 ml) and Na NO_2 (1 g) was added. The solution was boiled under reflux for 1.5 hr during which time the colour slowly changed from purple-red to orange-yellow. The hot solution was slowly poured into 1:1 acetone/2-propanol (50 ml) containing 12 F HCl (1 ml) and $ZnCl_2$ (1 g). After standing at 0-5° for 24 hours, the yellow product, that was slowly deposited, was collected, washed with acetone and then ether. The yield was 55.4%.

π-Nitro(ethylenediamine)(diethylenetriamine)cobalt(III) Tetrabromozincate(II): π-$[Co(en)(dien)Cl]ZnCl_4$ (1 g) was dissolved in 0.2 F HBr (25 ml) and $NaNO_2$ (3 g) was added. The solution was heated on a steam bath (ca. 80°) for 30 min. during which time there was mild effervescence and the colour changed from red to orange-yellow. The hot solution was slowly poured into 1:1 acetone/2-propanol containing 63% HBr (1 ml) and $ZnBr_2$ (2.5 g). The yellow product, that was deposited slowly on cooling at 0-5° for 24 hours, was collected, washed with acetone and then ether. The yield was 37.6%.

ω, *K* and π-Nitro(ethylenediamine)(diethylenetriamine) cobalt(III) Tetrathiocyanatozincate(II): The ω, *K* and π isomers of $[Co(en)(dien)NO_2]ZnCl_4$ (0.25 g) were separately dissolved in 0.2 F CH_3CO_2H (40 ml) at 60° and NH_4NCS (1.5 g) dissolved in water (6 ml) containing $Zn(CH_3CO_2)_2$ (1 g) was added. On standing at room temperature, the products were deposited as yellow crystal needles. The products were collected from the ice cooled solutions, washed with 2-propanol and then air dried. The yields were ω 93.7%, *K* 81.8%, π 95.3%.

ω, *K* and π-Isothiocyanato(ethylenediamine)(diethylene-triamine)cobalt(III) Tetrathiocyanatozincate(II): The ω, *K* and π isomers of $[Co(en)(dien)Cl]ZnCl_4$ (0.5 g, 0.25 g, 0.5 g respectively) were separately dissolved in 0.2 F CH_3CO_2H (65 ml, 32.5 ml, 65 ml) and NH_4NCS (2 g, 1 g, 2 g) was added. The red solutions, together with the crystalline tetrathiocyanatozincate(II) salts that were deposited, were refluxed for one hour. On cooling the solutions at 0-5° for 24 hours, the orange products that were slowly deposited were collected, washed with 2-propanol and then ether. The yields were ω 83.7%, *K* 78.6%, π 80.1%.

π-Isothiocyanato(ethylenediamine)(diethylenetriamine) cobalt(III) Tetrachlorozincate(II): π-[Co(en)(dien)NCS] $Zn(NCS)_4$ (0.1 g) was dissolved in acetone (5 ml) and 12 F HCl (1 ml) was added. The mixture was cooled in an ice bath and then a solution of 2-propanol (5 ml) containing $ZnCl_2$ (2 g) was added. On standing overnight, orange crystals were deposited and these were collected, washed with 2-propanol and then ether. The yield was 88.3%.

K and π-Formato(ethylenediamine)(diethylenetriamine) cobalt(III) Tetrachlorozincate(II): The *K* and π isomers of $[Co(en)(dien)Cl]ZnCl_4$ (0.25 g) were separately dissolved in 0.2 F HCl (12.5 ml) and NH_4COOH (2 g) was added. The solution was heated on a steam bath (ca. 80°) for 30 min. during which time the colour changed from red to orange. The hot solutions were slowly poured into 1:1 acetone/2-propanol (50 ml) containing 12 F HCl (0.5 ml) and $ZnCl_2$ (2 g). The solutions were cooled to 0-5° and after 24 hours the orange products, that were slowly deposited, were collected, washed with 2-propanol and then ether. The yields were *K* 49.4%, π 68.6%. The *K* isomer was also obtained when ω-$[Co(en)(dien)Cl]ZnCl_4$ was used as the starting material.

K and π-Formato(ethylenediamine)(diethylenetriamine) cobalt(III) Tetrathiocyanatozincate(II): The *K* and π isomers of $[Co(en)(dien)O_2CH]ZnCl_4$ (0.05 g) were separately dissolved in 0.2 F CH_3CO_2H (12.5 ml) and a solution of NH_4NCS (1 g) in water (2 ml) was added. The solution was allowed to stand at 0-5° for three days. The orange products, that were slowly deposited were collected, washed with 2-propanol and then air dried. The yields were *K* 78.2%, π 62.4%.

K and π-Acetato(ethylenediamine)(diethylenetriamine) cobalt(III) Tetrachlorozincate(II): The *K* and π isomers of $[Co(en)(dien)Cl]ZnCl_4$ (0.25 g) were separately dissolved in 0.2 F CH_3CO_2H (12.5 ml) and $CH_3CO_2NH_4$ (2.5 g) was added. The solutions were heated on a steam bath (ca. 80°) for 30 min. during which time the colour changed from red to orange. The hot solutions were slowly poured into 1:1 acetone/2-propanol (50 ml) containing 12 F HCl (0.5 ml) and $ZnCl_2$ (2.5 g). After standing the solutions at 0-5° for 2 days, the well formed orange crystals that were slowly deposited were collected, washed with 2-propanol and then ether. The yields were *K* 70.3%, π 25.1%. The *K* isomer was again obtained when ω-$[Co(en)(dien)Cl]ZnCl_4$ was used as the starting material.

K-Acetato(ethylenediamine)(diethylenetriamine)cobalt(III) Tetrathiocyanatozincate(II): *K*-$[Co(en)(dien)O_2CMe]ZnCl_4$ (0.05 g) was dissolved in 0.2 F CH_2CO_2H (15 ml) at 60° and a solution of NH_4NCS (1 g) in water (5 ml) was added. After standing the solutions at 0-5° for 24 hours, the orange product that was deposited was collected, washed with 2-propanol and then air dried. The yield was 95%.

K-Cinnamato(ethylenediamine)(diethylenetriamine) cobalt(III) Tetrathiocyanatozincate(II): *K*-$[Co(en)(dien)Cl](ClO_4)_2$ (0.25 g) was dissolved in 0.05 F HCl (12.5 ml) and $HO_2C(CH)_2Ph$ was added. The solution was heated on a steam bath (ca. 80°) for 30 min. during which time the colour changed from red to orange. After cooling to room temperature, NH_4NCS (5 g) and $ZnCl_2$ (2.5 g) were added to the solution and the pale orange product that deposited was collected, washed with 2-propanol and then air dried. The yield was 55.3%.

π-Lactato(ethylenediamine)(diethylenetriamine)cobalt(III) Tetrathiocyanatozincate(II): π-$[Co(en)(dien)Cl]ZnCl_4$ (0.25 g) was dissolved in 0.1 F $HClO_4$ (10 ml) and $KO_2CCH(OH)Me$ (2 g) was added. The solution was heated on a steam bath (ca. 80°) for 30 min. The solution was cooled to room temperature and then $ZnCl_2$ (4 g) and NH_4NCS (6 g) were added. After 24 hours, the orange-

yellow crystals that were slowly deposited were collected, washed with 2-propanol and then air dried. The yield was 69.2%.

K-Benzoato(ethylenediamine)(diethylenetriamine)cobalt(III) Tetrachlorozincate(II): *K*-$[Co(en)(dien)Cl](ClO_4)_2$ (0.25 g) was dissolved in 0.2 F HCl (20 ml) and NH_4O_2CPh (2.5 g) was added. The initial deposit of benzoic acid dissolved on heating the solution on a steam bath (ca. 80°) for 30 min. during which time the colour changed from red to orange. The solution was cooled to room temperature and the benzoic acid that was deposited was filtered off. 12 F HCl (0.5 ml) and $ZnCl_2$ (2.5 g) were added to the filtrate and the solution was stood at room temperature for 1 week. The product together with benzoic acid was then collected, washed with acetone, in which the benzoic acid was soluble, 2-propanol and then ether. The yield was 57.3%.

K-Benzoato(ethylenediamine)(diethylenetriamine)cobalt(III) Tetrathiocyanatozincate(II): *K*-$[Co(en)(dien)O_2CPh]ZnCl_4$ (0.1 g) was dissolved in water (5 ml) and NH_4NCS (2 g) and $ZnCl_2$ (1 g) were added. On cooling the solution in an ice bath the orange crystalline product that deposited was collected, washed with 2-propanol and then air dried. The yield was 82.1%.

π-Hydroxo(ethylenediamine)(diethylenetriamine)cobalt(III) Perchlorate: π-[Co(en)(dien)Cl]$ZnCl_4$ (4 g) and Ag_2O (4.8 g) were suspended in water (100 ml). The mixture was warmed (ca. 60°) for 15 min. and then filtered. $NaClO_4.H_2O$ (12 g) was added to the filtrate and the red-orange solution was evaporated to ca. 20 ml at 25° under a slow stream of air. The orange product that was slowly deposited, was collected and washed with methanol. The yield was 30%.

π-Aquo(ethylenediamine)(diethylenetriamine)cobalt(III) Perchlorate: π-[Co(en)(dien)Cl]$ZnCl_4$ (2 g) and Ag_2O (2.4 g) were suspended in water (50 ml) and the mixture was warmed (ca. 60°) for 15 min. and then filtered. The solution was made acid (pH 2) by the dropwise addition of 3 F $HClO_4$ and then $NaClO_4.H_2O$ (8 g) was added. The orange solution was evaporated to about 15 ml at ca. 25° under a stream of air. The orange product that was slowly deposited was collected and washed with methanol. The yield was 45%.

π-Nitrato(ethylenediamine)(diethylenetriamine)cobalt(III) Perchlorate: π-[Co(en)(dien)Cl]$ZnCl_4$ (0.25 g) was dissolved in water (5 ml) and $AgNO_3$ (0.25 g) was added. The solution was heated on a steam bath (ca. 80°) for 30

min. and it was then filtered. The filtrate was boiled for 30 min. in the presence of HNO_3 (15 F, 10 drops) and the orange solution was filtered and then evaporated slowly at room temperature to ca. 2 ml and then $NaClO_4.H_2O$ (2.5 g) dissolved in water (3 ml) was added. On standing at room temperature, the orange product was slowly deposited and it was collected and washed with acetone. The yield was 42.1%.

π-Chloro(ethylenediamine)(diethylenetriamine)chromium(III) Tetrachlorozincate(II): Green cis-Cr(dien)Cl_3 (2 g) was suspended in water (20 ml) and ethylenediamine (1 ml, 100%) was added. The solution was heated on a steam bath (ca. 80°) for 20 min. during which time the neutral complex dissolved giving a purple-violet solution. After cooling the solution in an ice bath for 10 min., 12 F HCl (10 ml) containing $ZnCl_2$ (2 g) was added. On standing the solution at 0-5° for two days the product deposited slowly and it was collected, washed with 2-propanol and then ether. The yield was 11%.

(2) 1,2-propanediamine

Analytical data for the complexes are presented in Table 2.8. Infrared spectra of the chloro $ZnCl_4^{2-}$ salts in the region 4000-400 cm^{-1} are presented in Fig. 2.2.

Table 2.3

Analytical Data for [Co(en)(dien)X-]Y

Complex	Calculated					Found				
	C%	H%	N%	Co%	X%[a]	C%	H%	N%	Co%	X%[a]
$[Co(en)(dien)Cl]ZnBr_4$ - ω				9.17	55.26				8.87	55.02
- K									9.25	55.12
- π									9.27	55.02
$[Co(en)(dien)Cl]Zn(NCS)_4$ - ω				10.61	48.20				10.61	48.12
- K									10.60	48.30
- π									10.64	48.12
$[Co(en)(dien)Cl]CoCl_4$ - π				25.71	38.67				25.68	38.51
$[Co(en)(dien)Cl]ZnI_4$ - π				7.10	65.38				7.01	65.49
$[Co(en)(dien)Cl]I_2$ - ω				11.52	56.55				11.79	56.01
- K									11.22	55.72
$[Co(en)(dien)Br]Br_2.H_2O$ - ω	15.02	4.83	14.59	12.28	49.95	16.23	4.94	14.44	12.39	49.33

Table 2.3 (contd.)

Complex	Calculated					Found				
	C%	H%	N%	Co%	X%[a]	C%	H%	N%	Co%	X%[a]
$[Co(en)(dien)Br]ZnBr_4$ - ω	10.49	3.08		8.58	58.15	10.88	3.10		8.59	57.81
- K						10.71	3.10		8.55	58.45
- π						10.40	2.97		8.69	58.31
$[Co(en)(dien)Br]ZnCl_4$ - ω				11.57	43.54				11.42	43.72
- K									11.51	43.44
- π									11.59	43.17
$[Co(en)(dien)Br]Zn(NCS)_4$ - ω				9.83	52.05				9.85	51.83
- K									9.72	51.55
- π									9.82	51.77
$[Co(en)(dien)Br]CdCl_4$ - K				10.60	39.85				10.52	39.71
$[Co(en)(dien)Br]CdBr_4$ - K				8.03	54.42				8.07	53.89
$[Co(en)(dien)Br](ClO_4)_2$ - K				11.76	15.95				11.72	15.89
- π									11.38	15.49
$[Co(en)(dien)I]I_2.H_2O$ - ω	11.61	3.73	11.28	9.49	61.31	12.23	3.75	11.76	9.50	61.05
- K						12.20	3.75		9.34	61.10

Table 2.3 (contd.)

Complex	Calculated					Found				
	C%	H%	N%	Co%	X%[a]	C%	H%	N%	Co%	X%[a]
$[Co(en)(dien)I]ZnCl_4$ - ω	12.96	3.81		10.60	48.30	13.00	4.09		10.72	47.93
- K						13.02	3.70		10.51	48.03
$[Co(en)(dien)I]ZnBr_4$ - ω				8.03	60.83				8.31	59.73
$[Co(en)(dien)I](ClO_4)_2$ - ω	13.15	3.86	12.78	10.75	23.16	12.88	4.00	12.63	10.39	23.25
$[Co(en)(dien)I]Zn(SCN)_4$ - ω				9.11	55.57				9.04	55.33
- K									9.03	55.29
$[Co(en)(dien)I]Br_2.H_2O$ - ω	13.91	4.28		11.38	55.36	14.25	4.26		11.36	55.03
$[Co(en)(dien)I]CdCl_4$ - ω				9.16	47.99				9.43	47.54
$[Co(en)(dien)I]CdBr_4$ - ω				7.54	57.18				7.55	56.85
$[Co(en)(dien)N_3]ZnBr_4$ - ω				9.08	49.23				9.22	48.92
- K									9.17	49.03
- π									9.07	49.21
$[Co(en)(dien)N_3]ZnCl_4$ - K	15.29	4.49	23.77	12.50	30.09	15.36	4.45	23.57	12.45	30.01
- π						15.13	4.57	23.41	12.37	30.13

Table 2.3 (contd.)

Complex	Calculated					Found				
	C%	H%	N%	Co%	X%[a]	C%	H%	N%	Co%	X%[a]
$[Co(en)(dien)N_3]Zn(NCS)_4$ - K				10.49	41.33				10.36	41.20
- π									10.40	41.10
$[Co(en)(dien)N_3]Cl.ClO_4$ - π				14.76	8.88				14.70	8.81
$[Co(en)(dien)N_3]CdBr_4$ - K				8.47	45.89				8.40	45.95
$[Co(en)(dien)NO_2]ZnCl_4$ - ω				12.40	29.83				12.74	29.31
- K									12.31	29.39
- π									12.35	29.79
$[Co(en)(dien)NO_2]ZnBr_4$ - π				9.02	48.93				8.99	48.89
$[Co(en)(dien)NO_2]Zn(NCS)_4$ - ω	21.22	3.74		10.41	41.05	21.55	3.73		10.47	40.59
- K						21.41	3.74		10.25	40.53
- π						21.43	3.83		10.35	40.82
$[Co(en)(dien)NCS]Zn(NCS)_4$ - ω	22.86	3.66	24.23	10.20	50.25	23.37	3.84	23.39	10.11	49.81
- K						22.99	3.71	23.42	9.89	50.03
- π						22.25	3.86	22.95	10.17	49.67
$[Co(en)(dien)NCS]ZnCl_4$ - π				12.09	40.02				11.87	39.81

Table 2.3 (contd.)

Complex	Calculated					Found				
	C%	H%	N%	Co%	X%[a]	C%	H%	N%	Co%	X%[a]
$[Co(en)(dien)O_2CH]ZnCl_4$ - κ	17.72	4.67		12.42	29.89	16.84	4.48		12.30	29.75
- π						16.68	4.34		12.25	29.60
$[Co(en)(dien)O_2CH]Zn(NCS)_4$ - κ				10.64	41.94				10.51	41.80
- π									10.45	41.70
$[Co(en)(dien)O_2CMe]ZnCl_4$ - κ				12.06	29.03				12.02	29.00
- π									12.15	29.10
$[Co(en)(dien)O_2CMe]Zn(NCS)_4$ - κ	23.30	4.27		10.40	40.98	24.05	4.43		10.31	40.75
$[Co(en)(dien)O_2C(CH)_2Ph]Zn(NCS)$ - κ				8.83	34.83				8.95	34.62
$[Co(en)(dien)O_2C(CH.OH)Me]Zn(NCS)_4$ - κ				9.69	38.21				9.55	38.40
$[Co(en)(dien)O_2CPh]ZnCl_4$ -	28.36	4.76		10.71	25.76	28.84	4.95		10.53	25.21
$[Co(en)(dien)O_2CPh]Zn(NCS)_4$ - κ				9.27	35.49				9.22	35.40
$[Co(en)(dien)OSO_2H]Zn(NCS)_4$ - π	19.99	3.69		9.81	48.60	19.22	4.03		9.75	48.45
$[Co(en)(dien)OH](ClO_4)_2$ - π	16.45	5.06		13.45		16.39	5.19		13.31	

Table 2.3 (contd.)

Complex	Calculated					Found				
	C%	H%	N%	Co%	X%[a]	C%	H%	N%	Co%	X%[a]
$[Co(en)(dien)OH_2](ClO_4)_3$ - π	13.38	4.30		10.94		13.20	4.21		10.88	
$[Co(en)(dien)NO_3](ClO_4)_2$ - π	14.92	4.38		12.20		14.80	4.51		12.05	
$[Co(en)(dien)Cl]ZnCl_4$ - π	15.74	4.62	15.30	11.36[b]	38.71	15.83	4.52	15.47	11.25[b]	38.91

[a] Total Halogen or NCS^- as found by Ag^+ titration.

[b] Cr%

μ-Peroxobis(1,2-propanediamine)bis(diethylenetriamine) dicobalt(III) Perchlorate Monohydrate: An aqueous solution (200 ml) of 1,2-propanediamine (7 g) and diethylenetriamine (10.5 g) was added to a stirred solution of $Co(NO_3)_2.6H_2O$ (30 g) in water (400 ml). A rapid stream of O_2 gas was passed through the stirred, room temperature solution and after 30 min., $NaClO_4.H_2O$ (30 g) was added. An oil was immediately formed and after a further 2 hours a brown solid was slowly deposited. $NaClO_4.H_2O$ (60 g) was then added and the brown solid material was then collected, washed with 2-propanol and then ether, and then air dried. On washing the surface of the initially formed oil solidification occurred and this product was collected, washed and dried as above. The total yield was 36 g or 72%.

A sample for analysis was prepared by dissolving 1 g of the crude material in the minimum volume (ca. 80 ml) of 0.1 F $HClO_4$ at 60°. Excess $NaClO_4.H_2O$ was added to the stirred solution and the brown crystalline product that deposited was collected, washed and dried as before. An 80% recovery was obtained.

Isomers of Chloro(1,2-propanediamine)(diethylenetriamine) cobalt(III) Tetrachlorozincate(II):

Method A: $[Co_2(pn)_2(dien)_2O_2](ClO_4)_4.2H_2O$ (35 g) was added to a solution of 12 F HCl (100 ml) in water (180 ml) con-

taining $ZnCl_2$ (50 g). The solution was heated on a steam bath (ca. 80°) until the effervescence ceased (1 hour), during which time a red crystalline material was deposited. This was collected from the hot solution, washed with 2-propanol and then ether. The crude product was recrystallised by dissolving it in the minimum volume of 0.2 F CH_3CO_2H at 60° (1 g/20 ml) and then adding 12 F HCl (10 ml/1 g) containing $ZnCl_2$ (2.5 g/1 g). The purified product that was deposited on cooling the solution to room temperature was collected in fractions and was washed and dried as above.

The aqueous mother liquor was reheated to 80° to evaporate it to ca. 300 ml.12 F HCl (50 ml) was then added to the solution and after standing at room temperature for 12 hours, further crops were deposited. These were recrystallised as above but using a corresponding reduction in the volumes and weights of the reagents used.

Further product was obtained on the slow evaporation of the aqueous mother liquor at room temperature (final volume 80 ml).

The total yield of chloropentaamine product was 14.90 g or 44.8%. The isomeric composition of each fraction of recrystallised product is listed in Table 2.4.

Method B: trans - $Co(dien)(NO_2)_3$ (28 g) was suspended in water (60 ml) and 1,2-propanediamine (8.0 ml, 100%)was

Table 2.4

Isomeric Compositions of $[Co(pn)(dien)Cl]ZnCl_4 \cdot xH_2O$; Method A

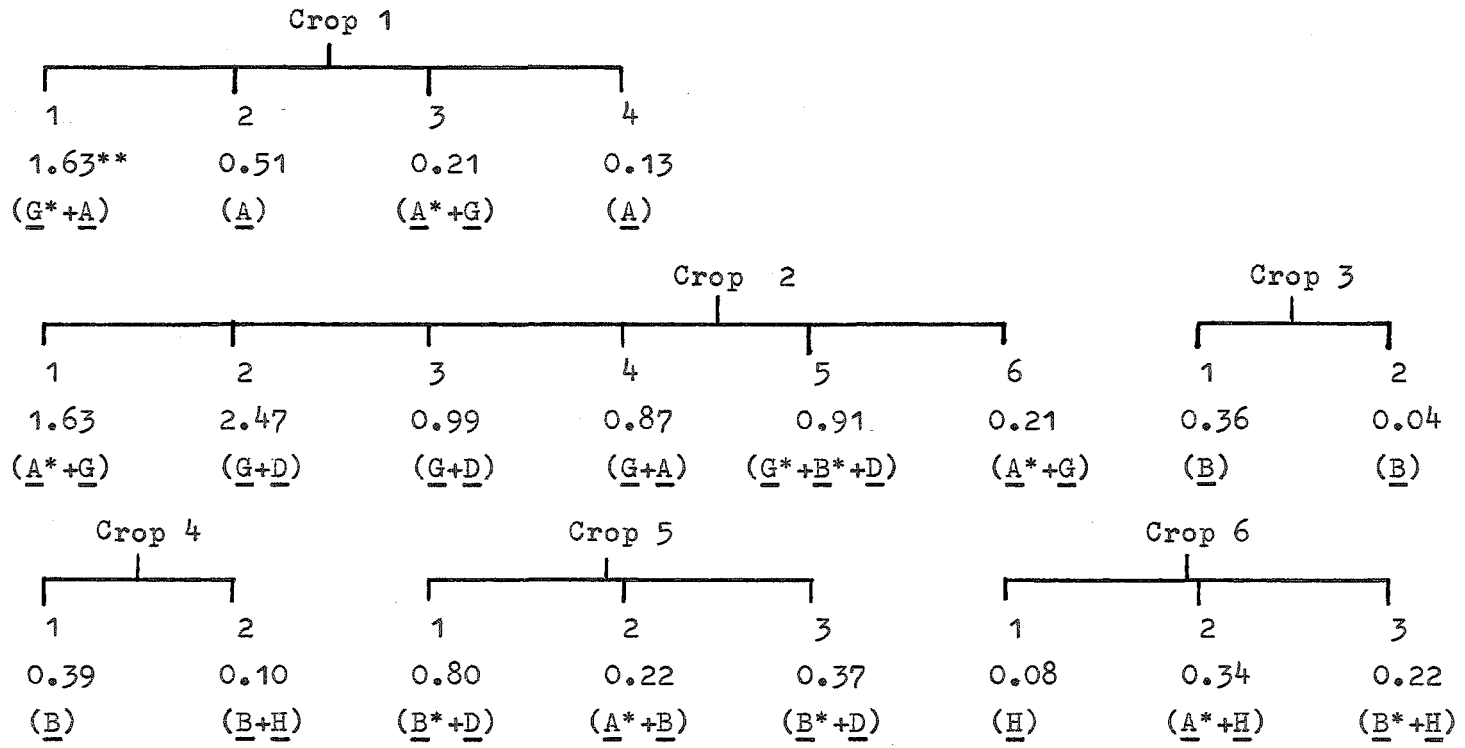
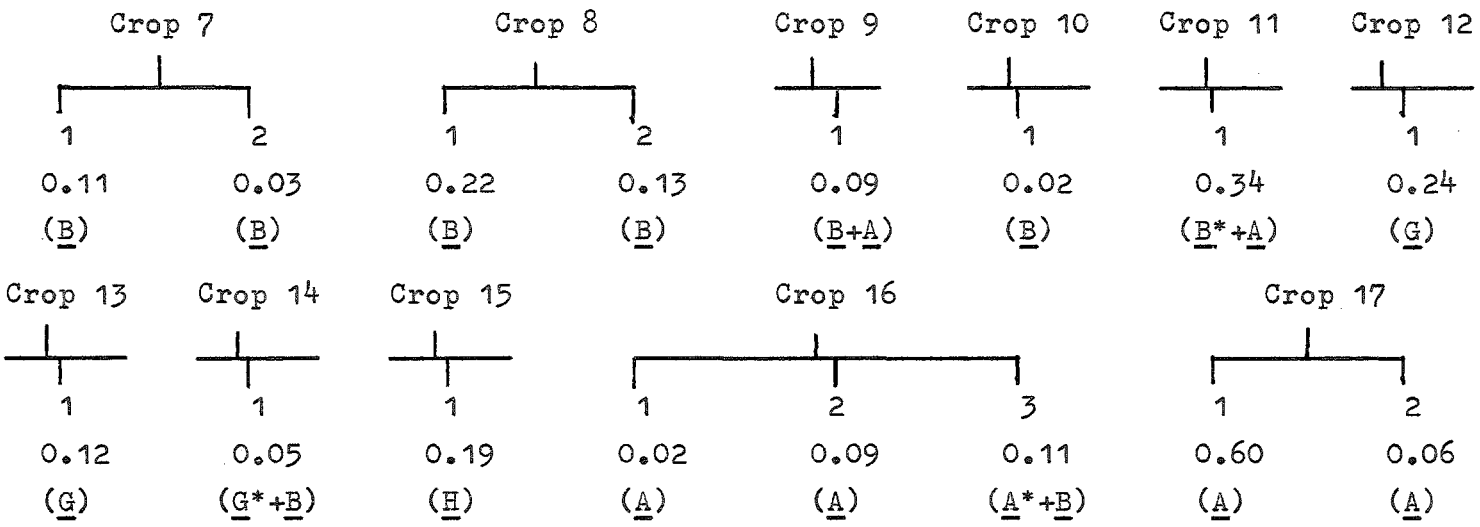


Table 2.4 (contd.)



* denotes major component(s) of fraction

** weight in g

added. The solution was stirred and allowed to digest the neutral complex on a steam bath at ca. 80°. After 30 mins, the dark brown solution was cooled in ice and 12 F HCl (30 ml) was slowly added. The solution was reheated for a further 45 min. and then $ZnCl_2$ (15 g) was added. The product that deposited on cooling was collected in crops, washed with 2-propanol and then ether. The crude complex was recrystallised by dissolving each crop in the minimum volume of 0.1 F HCl (1 g/50 ml) at 60° and then adding 12 F HCl (10 ml/1 g) containing $ZnCl_2$ (2.5 g/1 g). The purified product that was deposited on cooling to room temperature was collected in fractions and was washed and dried as above.

The aqueous mother liquor deposited further crops on slow evaporation at room temperature. These were recrystallised as above but using a corresponding reduction in the weights and volumes of the reagents used.

The total yield of chloropentaamine complex was 16.00 g or 35.8%. The isomeric composition of each fraction of recrystallised product is listed in Table 2.5.

Method C: trans - $Co(dien)(NO_2)_3$ (14 g) was suspended in water (30 ml) and 1,2-propanediamine (4.3 ml, 100%) was added. The mixture was heated on a steam bath (ca. 80°) until the neutral complex dissolved to give a dark brown solution. After cooling the solution in an ice bath, 12 F

Table 2.5

Isomeric Compositions of Fractions of $[Co(pn)(dien)Cl]ZnCl_4 \cdot xH_2O$; Method B

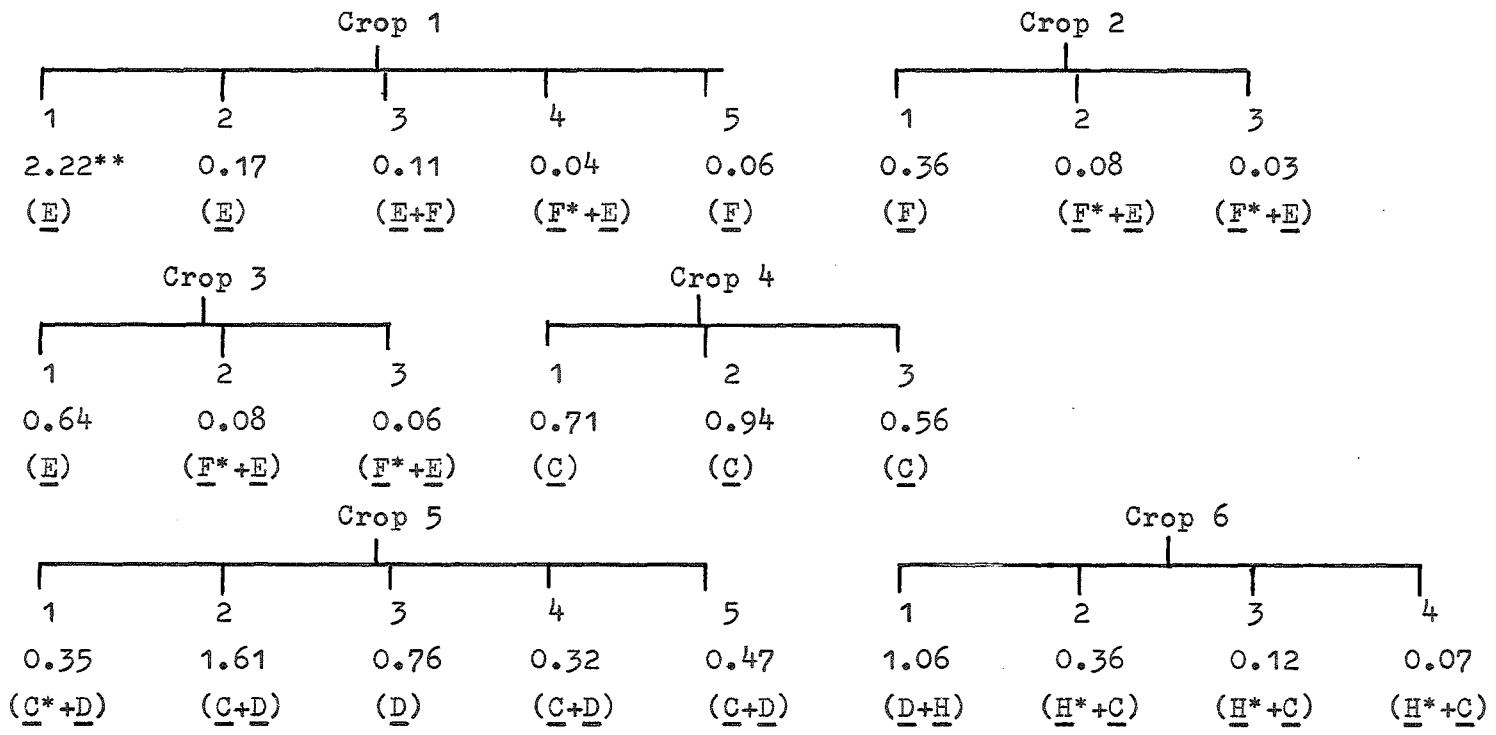
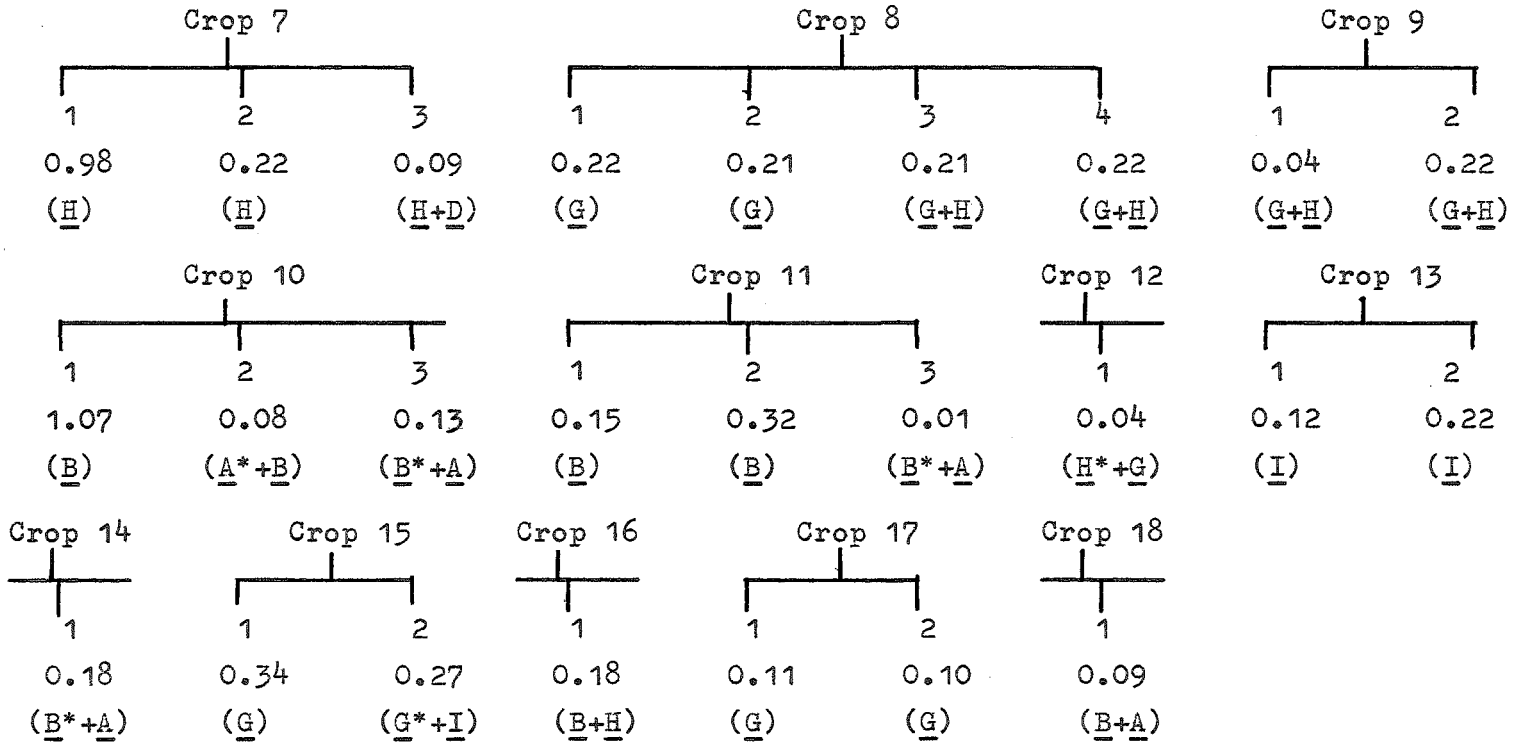


Table 2.5 (contd.)



* denotes major component(s) of fraction

** weight in g

HCl (25 ml) was slowly added. The solution was reheated for a further 3 hours during which time a dark red colour formed. 12 F HCl (25 ml) containing $ZnCl_2$ (15 g) was then added and the crystalline product that deposited on cooling to room temperature was collected in crops, washed with 2-propanol and then ether. The crude product was recrystallised by dissolving it in 0.2 F CH_3CO_2H (1 g/25 ml) at 60° and then adding 12 F HCl (10 ml/1 g) containing $ZnCl_2$ (2.5 g/1 g). The purified product that deposited on cooling to room temperature was collected in fractions, washed and dried as above.

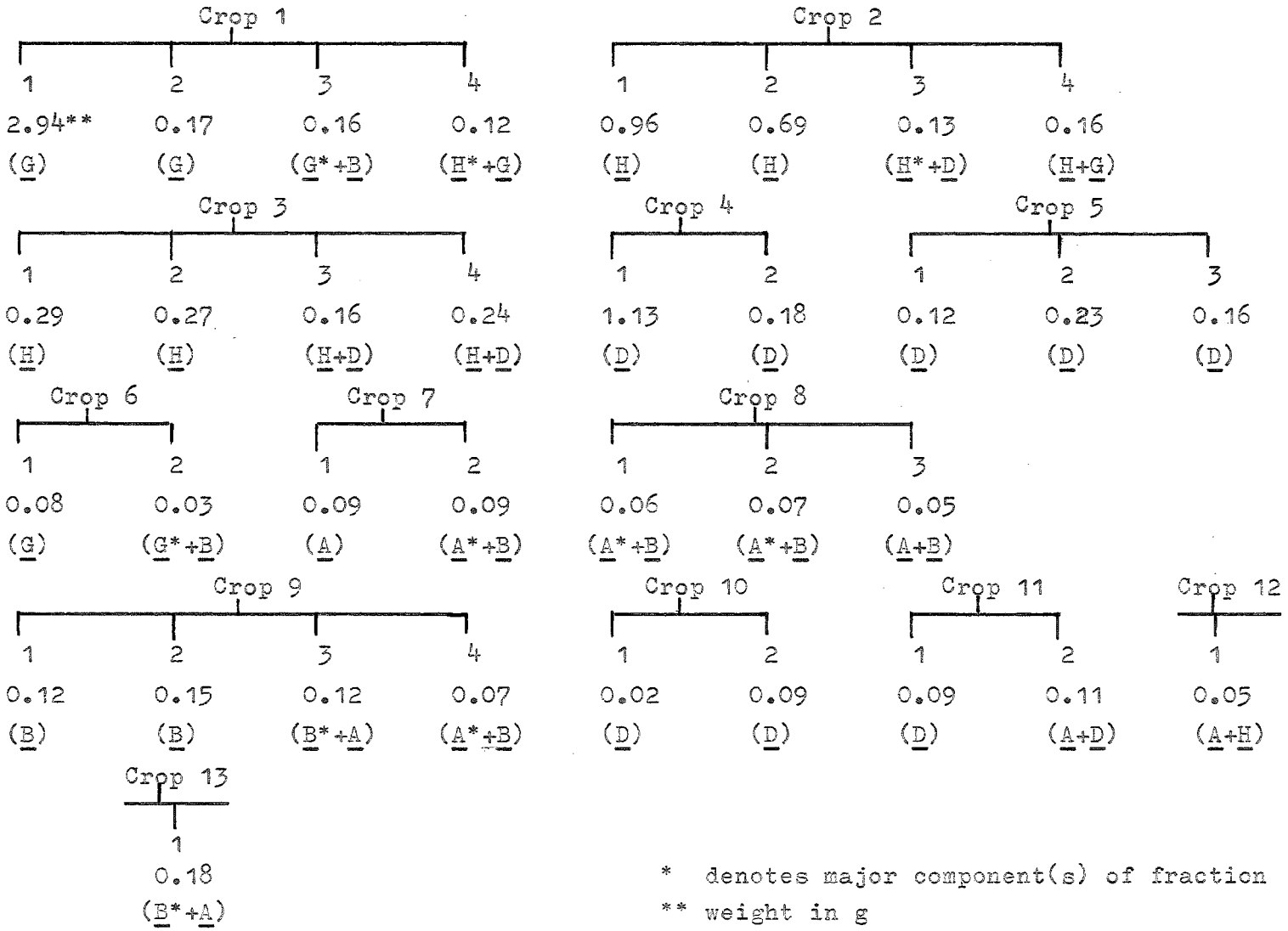
The aqueous mother liquor was reheated for a further 1.5 hours and then 12 F HCl (25 ml) containing $ZnCl_2$ (5 g) was added. The product, that was deposited slowly, was collected in crops and was recrystallised as above but using a corresponding reduction in the weights and volumes of the reagents used.

The total yield of chloropentaamine product was 9.58 g or 43.2%. The isomeric composition of each fraction of recrystallised product is listed in Table 2.6.

Qualitative Isomerisation Reactions: Small quantities of the pure isomers were taken and subjected to the following chemical reactions. The isomeric composition of the chloro $ZnCl_4^{2-}$ and the nitro $ZnCl_4^{2-}$ salts was determined by

Table 2.6

Isomeric Composition of fractions of $[Co(pn)(dien)Cl]ZnCl_4 \cdot xH_2O$; Method C.



* denotes major component(s) of fraction

** weight in g

examination of the infrared spectrum.

(a) Reaction with Nitrous Acid: Nitro compounds derived from the A, B, C, D, "E", "F", G, H and I isomers of $[Co(pn)(dien)Cl]ZnCl_4.xH_2O$ were prepared using the method described later. The products were decomposed by heating a solution of each in 3 F HCl on a steam bath (ca. 80°) for 1 hour. The $ZnCl_4^{2-}$ salts of the chloro isomers generated in this manner were deposited by the addition of $ZnCl_2$. The transformations that resulted were:

A → A+G; B → B+D; C → C; D → D+B; "E" → A+G; "F" → A+G; G → A+G; H → H; I → I.

(b) Base Hydrolysis: The A, B, C, D, "E", "F", G, H and I isomers of $[Co(pn)(dien)Cl]ZnCl_4.xH_2O$ were separately dissolved in water (0.25 g/10 ml) and 1 F NaOH (10 ml) was added. The solutions were heated at 70° for 20 min. and then 12 F HCl (10 ml) containing $ZnCl_2$ (4 g) was added. The solutions were left to stand at room temperature overnight and the product was collected, washed with 2-propanol and then ether. The results were: A → A+G; B → B+D; C → B+D; D → D+B; "E" → A+G; "F" → A+G; G → G+A; H → G+A; I → B+D.

(c) Reflux in 6 F HCl: The pure isomers of $[Co(pn)(dien)Cl]ZnCl_4.xH_2O$ were separately dissolved in 6 F HCl (0.2 g/25 ml) and the solutions were boiled under

reflux for one hour. 12 F HCl (15 ml) containing $ZnCl_2$ (5 g) was then added and the products that were slowly deposited from the ice cooled solutions were collected, washed with 2-propanol and then ether. The results were A → A; B → B; C → C; D → D; "E" → A; "F" → G; G → G; H → H; I → I.

A, B, C, D, G and H - Chloro(1,2-propanediamine)(diethylenetriamine)cobalt(III) Tetrabromozincate(II): The A, B, C, D, G and H isomers of $[Co(pn)(dien)Cl]ZnCl_4.xH_2O$ were separately dissolved in 0.2 F CH_3CO_2H (0.25 g/25 ml, 0.25 g/25 ml, 0.25 g/25 ml, 0.25 g/10 ml, 0.25 g/10 ml, 0.25 g/25 ml respectively) and a solution of 50% HBr (10 ml, 10 ml, 10 ml, 10 ml, 10 ml, 15 ml) containing $ZnBr_2$ (2.5 g, 2.5 g, 2.5 g, 4 g, 2.5 g, 4 g) was added. The products that were deposited immediately were collected from the ice cooled solutions, washed with 2-propanol and then ether. The yields were A 75.8%, B 84.4%, C 66.9%, D 68.2%, G 76.2% and H 61.1%.

B, G and H - Chloro(1,2-propanediamine)(diethylenetriamine)cobalt(III) Tetrabromocadmiumate(II): The B, G and H isomers of $[Co(pn)(dien)Cl]ZnCl_4.xH_2O$ were separately dissolved in 0.2 F CH_3CO_2H (0.25 g/25 ml, 0.5 g/30 ml, 0.1 g/10 ml, respectively) and a solution of 50% HBr (10 ml, 40 ml, 15 ml) containing $CdBr_2.4H_2O$ (2.5 g, 5 g, 2.5 g) was added. The crystalline products that were deposited slowly were

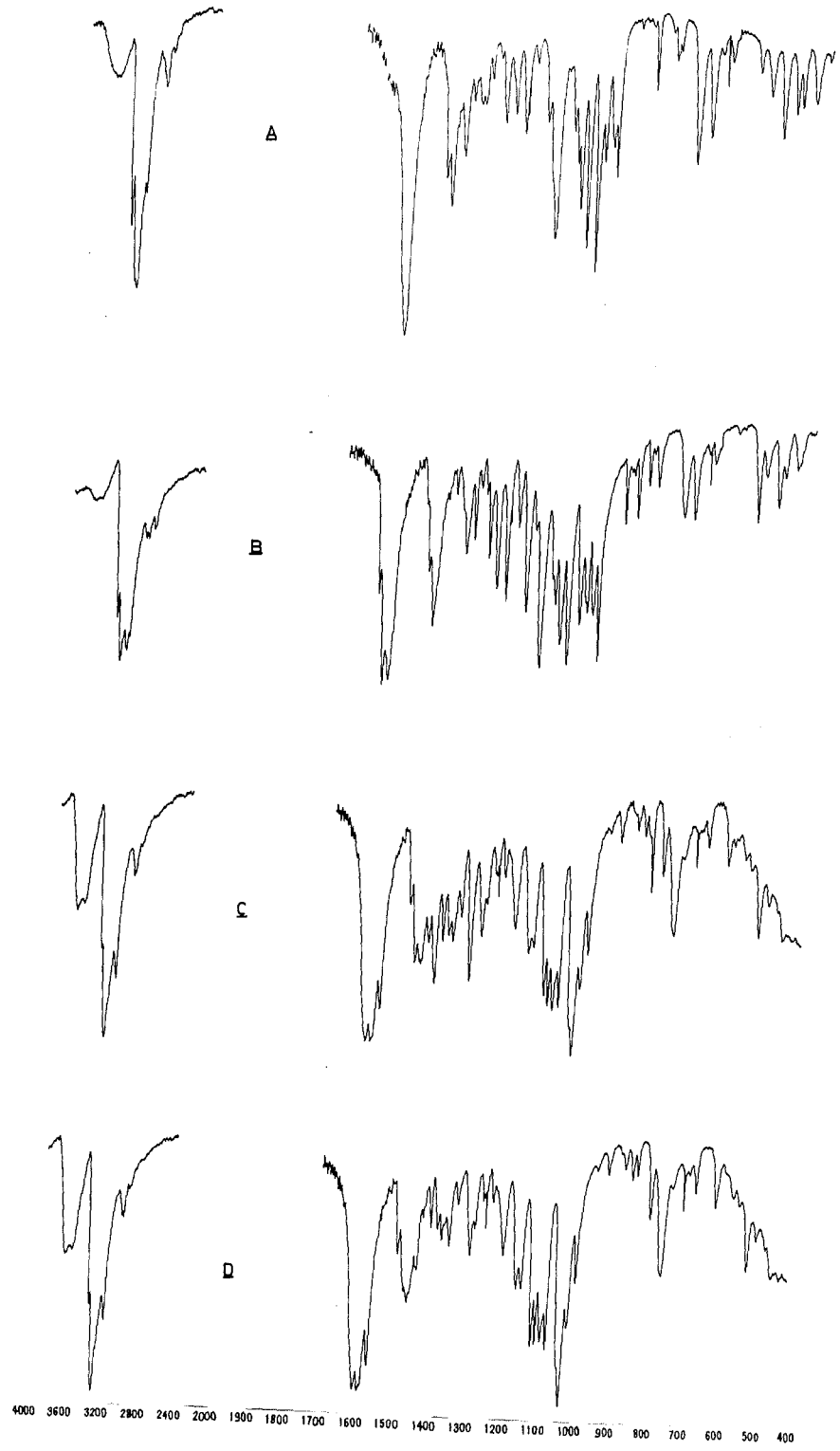
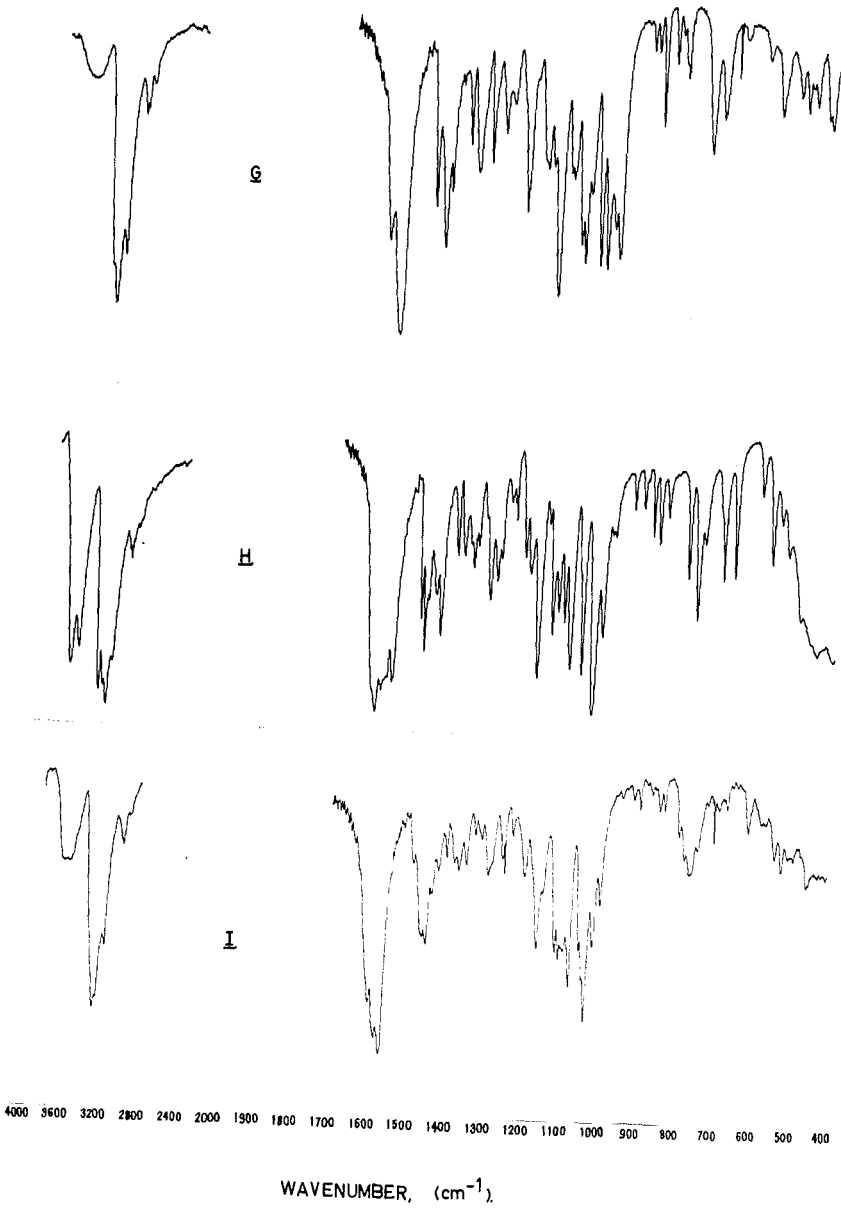


Figure 2.2 Infrared spectra of A, B, C and D - $[Co(pn)(dien)]ZnCl_4.xH_2O$ in the range 4000-400 cm^{-1} (KBr Disc).

Figure 2.3 Infrared spectra of G, H and I - $[Co(pn)(dien)Cl]ZnCl_4 \cdot xH_2O$ in the range 4000-400 cm^{-1} (KBr Disc).



collected from the ice cooled solutions, washed with 2-propanol and then ether. The yields were B 79.8%, G 80.6%, and H 42.2%.

A, B, D, G and H - Chloro(1,2-propanediamine)(diethylenetriamine)cobalt(III) Tetrathiocyanatozincate(II): The A, B, D, G and H isomers of $[Co(pn)(dien)Cl]ZnCl_4.xH_2O$ were separately dissolved in 0.2 F CH_3CO_2H (0.15 g/15 ml, 0.25 g/30 ml, 0.25 g/30 ml, 0.25 g/30 ml, 0.25 g/40 ml, respectively) and NH_4NCS (1.5 g, 2.5 g, 2 g, 2.5 g, 2.5 g) was added. The products, that were slowly deposited on cooling the solutions in an ice bath, were collected, washed with 2-propanol and then ether. The yields were A 80.3%, B 88.4%, D 79.4%, G 70.5% and H 77.9%

A, B and G - Chloro(1,2-propanediamine)(diethylenetriamine)cobalt(III) Perchlorate: The A, B and G isomers of $[Co(pn)(dien)Cl]ZnCl_4$ (1 g, 0.5 g, 0.25 g respectively) were separately dissolved in the minimum volume of 3 F $HClO_4$ at 60° (35 ml, 15 ml, 8 ml) and $NaClO_4.H_2O$ (10 g, 5 g, 2 g) was added. The red crystalline products that were deposited on cooling the solutions in an ice bath were collected, washed with 2-propanol and then ether. The yields were A 63.2%, B 83.4%, and G 76.7%.

Attempts to prepare the perchlorate salts of the H and D isomers were unsuccessful.

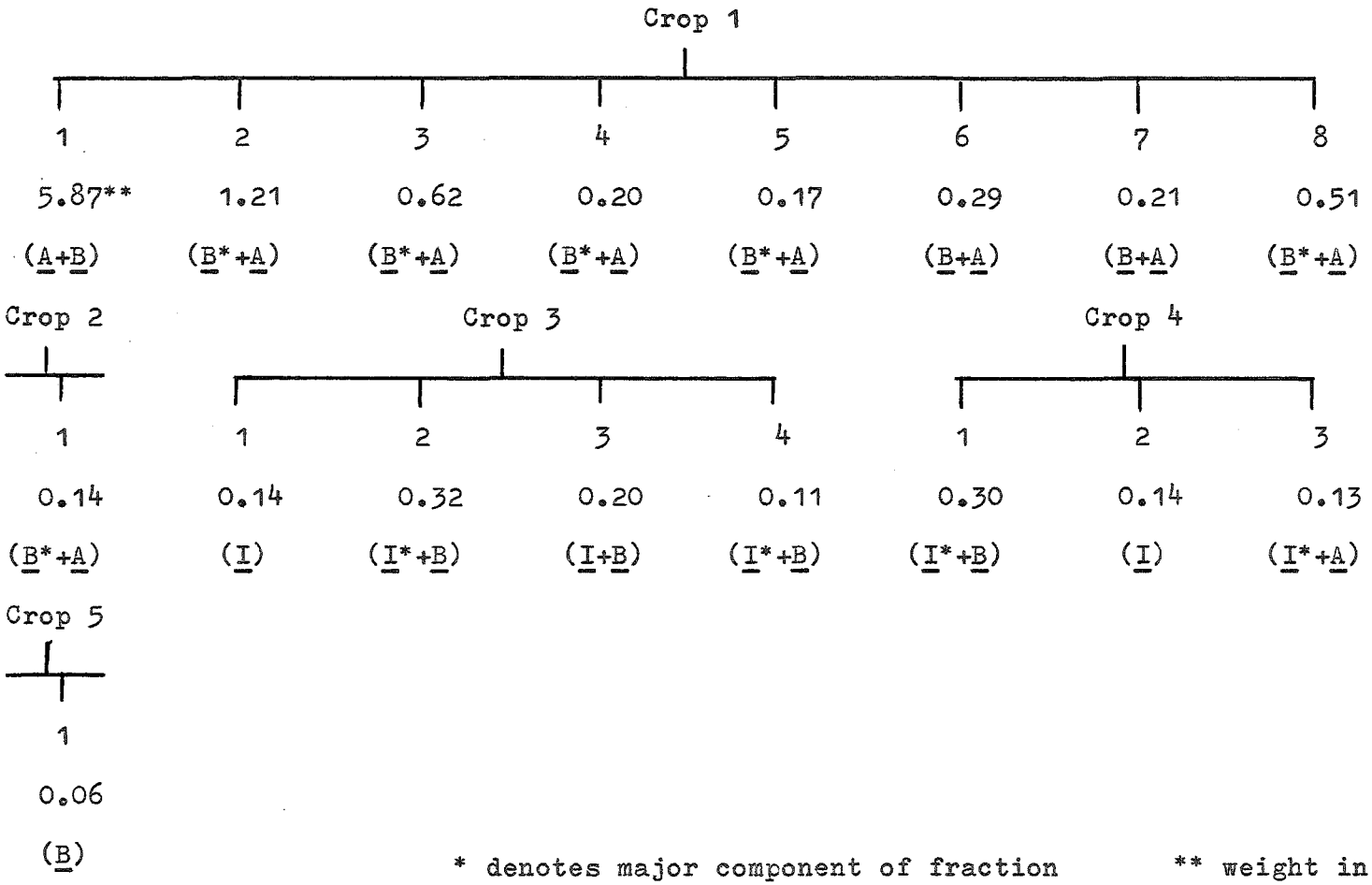
Isomers of Bromo(1,2-propanediamine)(diethylenetriamine) cobalt(III) Tetrabromozincate(II): $[Co_2(pn)_2(dien)_2O_2](ClO_4)_4.H_2O$ (12 g) was suspended in water (60 ml) and 63% HBr (30 ml) was added. The mixture was heated on a steam bath (ca. 80°) for 15 min. and then $ZnBr_2$ (5 g) was added. The heating was continued for a further 15 min during which time the purple crystalline product was deposited. After cooling to room temperature, the crude product was collected, washed with 2-propanol and then ether. The crude product was recrystallised by dissolving it in 0.2 F CH_3CO_2H (1 g/15 ml) at 60° and then adding 40% HBr (5 ml/1 g) containing $ZnBr_2$ (2.5 g/1 g). The product that deposited on cooling to room temperature was collected in fractions and was washed and dried as above.

The aqueous mother liquor yielded further crops of crude product on slow evaporation at room temperature and these were recrystallised as above but using a corresponding reduction in the weights and volumes of the reagents used.

The total yield of bromopentaamine product was 10.62 g or 63.1%. The isomeric composition of the fractions is listed in Table 2.7. The A isomer can be separated by careful fractional crystallisation of a mixture containing a high percentage of this isomer.

Table 2.7

Isomeric Compositions of $[Co(pn)(dien)Br]ZnBr_4 \cdot xH_2O$



* denotes major component of fraction ** weight in g.

B, G and H - Bromo(1,2-propanediamine)(diethylenetriamine) cobalt(III) Tetrabromozincate(II): The B, G and H isomers of $[Co(pn)(dien)Cl]ZnCl_4.xH_2O$ were separately dissolved in water (0.5 g/10 ml, 0.5 g/25 ml, 0.5 g/25 ml, respectively) and 63% HBr (2 ml, 5 ml, 8 ml) was added. The solutions were boiled under reflux for (30 min, 5 hours, 2 hours) during which time the colour changed from red to purple. The hot solutions were added to solutions of 63% HBr (5 ml, 10 ml, 10 ml) in water (10 ml) containing $ZnBr_2$ (2 g, 2.5 g, 2.5 g). On cooling to room temperature the crystalline purple products were deposited and these were collected from the ice cooled solutions washed with 2-propanol and then ether. The yields were B 46.2%, G 50.3% and H 74.0%.

D - Bromo(1,2-propanediamine)(diethylenetriamine)cobalt(III) Tetrabromocadmiumate(II): D - $[Co(pn)(dien)Cl]ZnCl_4.\frac{3}{2}H_2O$ (0.5 g) was dissolved in water (20 ml) and 50% HBr (15 ml) was added. The solution was boiled under reflux for 20 min. during which time the colour changed from red to purple. The hot solution was slowly poured into 50% HBr (20 ml) containing $CdBr_2.4H_2O$ (4 g). The purple product, that was deposited on cooling the solution to room temperature, was collected in fractions and washed with ether. The yield was 65.3%. The first fraction contained an appreciable percentage of the B isomer.

A, B and H- Bromo(1,2-propanediamine)(diethylenetriamine) cobalt(III) Tetrabromocadmiumate(II): The A, B and H isomers of $[Co(pn)(dien)Br]ZnBr_4.xH_2O$ were separately dissolved in 0.2 F CH_3CO_2H (0.25 g/20 ml, 0.25 g/20 ml, 0.1 g/10 ml, respectively) at room temperature and a solution of 50% HBr (10 ml, 10 ml, 10 ml) containing $CdBr_2.4H_2O$ (2.5 g, 2.5 g, 1 g) was added. The purple crystalline products were immediately deposited and they were collected, washed with 2-propanol and then ether. The yields were A 90.3%, B 72.6% and H 75.4%.

B - Bromo(1,2-propanediamine)(diethylenetriamine)cobalt(III) Tetrachlorozincate(II): B - $[Co(pn)(dien)Br]ZnBr_4$ (0.25 g) was dissolved in 0.2 F CH_3CO_2H (25 ml) at 40° and a solution of 12 F HCl (10 ml) containing $ZnCl_2$ (2.5 g) was added. The purple crystalline product, that was slowly deposited on cooling to room temperature, was collected from the ice cooled solution, washed with 2-propanol and then ether. The yield was 91.3%.

G and H - Iodo(1,2-propanediamine)(diethylenetriamine) cobalt(III) Tetrachlorozincate(II): A mixture of the G and H isomers of $[Co(pn)(dien)Cl]ZnCl_4.xH_2O$ (2 g) was dissolved in water (20 ml) and NaI (5 g) was added. The solution was heated on a steam bath (ca. 80°) for one hour and it was then cooled to room temperature. The iodine that was

deposited was removed by filtration. After standing the filtrate for 48 hours at room temperature, the green product that was slowly deposited was collected, washed with acetone and then ether. The crude product was converted to the tetrachlorozincate(II) salt by dissolving it in water (0.1 g/40 ml) and then adding 12 F HCl (10 ml/0.1 g) containing $ZnCl_2$ (2.5 g, 0.1 g). The purified product, that was deposited immediately, was collected, washed with 2-propanol and then ether.

Two fruther crops were obtained from the aqueous mother liquor and these were recrystallised as above but using a corresponding reduction in the weights and volumes of the reagents used.

The yield was 0.23 g or 10.0%. The first two crops were the G isomer and the last crop the H isomer.

A - Azido(1,2-propanediamine)(diethylenetriamine)cobalt(III) Tetrachlorozincate(II): A - $[Co(pn)(dien)Cl]ZnCl_4$ (1 g) was dissolved in 0.2 F CH_3CO_2H (20 ml) and NaN_3 (3 g) was added. The solution was heated on a steam bath (ca. 80°) for 20 min. and then it was cooled to room temperature. The solution was added to 1:1 2-propanol/methanol (100 ml) and the purple-red product, that was deposited slowly on cooling in an ice bath, was collected, washed with 2-propanol and then ether. The yield was 80.0%.

G and H - Azido(1,2-propanediamine)(diethylenetriamine) cobalt(III) Tetrabromocadmiumate(II): The G and H isomers of $[Co(pn)(dien)Cl]ZnCl_4.xH_2O$ were separately dissolved in 0.2 F CH_3CO_2H (0.75 g/35 ml, 0.5 g/25 ml respectively) and NaN_3 (3g, 2.5 g) was added. The solutions were boiled under reflux for 20 min. and then the hot solutions were slowly poured into 50% HBr (15 ml, 10 ml) containing $CdBr_2.4H_2O$ (4 g, 2.5 g). On cooling the solutions in an ice bath, the purple-red products were slowly deposited. These were collected, washed with 2-propanol and then ether. The yields were G 32.8% and H 16.8%.

A - Azido(1,2-propanediamine)(diethylenetriamine)cobalt(III) Tetrabromozincate(II): A - $[Co(pn)(dien)N_3]ZnCl_4$ (0.25 g) was dissolved in 0.2 F CH_3CO_2H (20 ml) and a solution of 63% HBr (10 ml) containing $ZnBr_2$ (2.5 g) was added. The crystalline product, that was deposited on cooling the solution in an ice bath, was collected, washed with 2-propanol and then ether. The yield was 72.0%.

A - Azido(1,2-propanediamine)(diethylenetriamine)cobalt(III) Tetrathiocyanatozincate(II): A - $[Co(pn)(dien)N_3]ZnCl_4$ (0.2 g) was dissolved in 0.2 F CH_3CO_2H (20 ml) and a solution of NH_4NCS (2.5 g) and $Zn(O_2CCH_3)_2$ (0.5 g) in water (15 ml) was added. The crystalline product was deposited immediately and it was collected from the ice cooled solution, washed

with 2-propanol and then air dried. The yield was 65.0%.

A, B, C, G and I - Nitro(1,2-propanediamine)(diethylenetriamine)cobalt(III) Tetrachlorozincate(II): The A, B, C, G and I isomers of $[Co(pn)(dien)Cl]ZnCl_4.xH_2O$ were separately dissolved in 0.2 F HCl (0.5 g/12.5 ml, 0.5 g/12.5 ml, 0.5 g/12.5 ml, 0.5 g/10 ml, 0.1 g/5 ml, respectively) and $NaNO_2$ (2 g, 2 g, 2 g, 2 g, 1 g) was added. The solutions were heated on a steam bath (ca. 80°) for 30 min. and then the hot solutions were slowly poured into 1:1 2-propanol/acetone (50 ml, 50 ml, 50 ml, 50 ml, 25 ml) containing 12 F HCl (1 ml, 1 ml, 1 ml, 1 ml, 0.25 ml) and $ZnCl_2$ (2.5 g, 2.5 g, 2.5 g, 2.5 g, 2 g). On cooling to room temperature, the orange-yellow products were slowly deposited and they were collected, washed with acetone and then ether. The yields were A 46.8%, B 66.2%, C 72.8%, G 51.2% and I 60.2%.

D and H - Nitro(1,2-propanediamine)(diethylenetriamine)cobalt(III) Tetrachlorozincate(II): The D and H isomers of $[Co(pn)(dien)Cl]ZnCl_4.xH_2O$ were separately dissolved in 0.2 F HCl (0.25 g/8 ml) and $NaNO_2$ (1 g) was added. The solutions were boiled under reflux for 15 min. and then were slowly poured into 1:1 2-propanol/acetone (25 ml) containing 12 F HCl (1 ml) and $ZnCl_2$ (2.5 g). On cooling the solutions to room temperature, the orange-yellow crystalline products were slowly deposited and they were collected, washed with

acetone and then ether. The yields were D 45.2% and H 43.2%.

A, B and G - Nitro(1,2-propanediamine)(diethylenetriamine) cobalt(III) Tetrathiocyanatozincate(II): The A, B and G isomers of $[Co(pn)(dien)NO_2]ZnCl_4$ were separately dissolved in 0.2 F CH_3CO_2H (0.15 g/12 ml, 0.2 g/15 ml, 0.25 g/25 ml, respectively) and NH_4NCS (1.5 g, 2 g, 2.5 g) was added. On cooling the solutions in an ice bath the products were slowly deposited, and these were collected, washed with 2-propanol and then ether. The yields were A 86.0%, B 77.8% and G 71.9%.

A and G - Isothiocyanato(1,2-propanediamine)(diethylene-triamine)cobalt(III) Tetrathiocyanatozincate(II): The A and G isomers of $[Co(pn)(dien)]Cl\ ZnCl_4$ were separately dissolved in 0.2 F CH_3CO_2H (1.5 g/60 ml, 0.25 g/30 ml respectively) and NH_4NCS (5 g, 1 g) was added. The red solutions together with the crystalline precipitates of the tetrathiocyanato-zincate(II) salts were heated on a steam bath (ca. 80°) for 45 min. The solutions were allowed to stand at room temperature and the products, that were slowly deposited, were collected, washed with 2-propanol and then ether. The yields were A 33.2% and G 45.7%.

B, D and H - Isothiocyanato(1,2-propanediamine)(diethylene-triamine)cobalt(III) Tetrathiocyanatozincate(II): The B, D and H isomers of $[Co(pn)(dien)Cl]ZnCl_4.xH_2O$ were separately dissolved in 0.2 F CH_3CO_2H (0.15 g/25 ml, 0.15 g/25 ml, 0.25 g/30 ml respectively) and NH_4NCS (1.5 g, 1 g, 2 g) was added. The solutions were boiled under reflux for 1 hour and then cooled to room temperature. The products, that were slowly deposited, were collected, washed with 2-propanol and then ether. The yields were B 50.6%, D 61.3% and H 41.7%.

Resolution of D - $Co(pn)(dien)Cl^{2+}$

D - $[Co(pn)(dien)Cl]ZnCl_4.\frac{3}{2}H_2O$ (0.5 g) was dissolved in water (10 ml) at 45° and 5 drops of glacial acetic acid were added. Ammonium $(+)_{589}$-α-Bromo-Camphor-π-Sulphonate, (+)BCS, (0.5 g) was slowly added in 0.1 g portions. The pink diastereoisomer complex that was immediately deposited was collected in two crops, washed with 2-propanol and then ether (Crops 1 and 2). A further 0.25 g portion of (+)BCS was then added and the pink precipitate that deposited was collected after 24 hours at room temperature and it was washed and dried as above (Crop 3).

12 F HCl (10 ml) containing $ZnCl_2$ (2.5 g) was then added to the aqueous mother liquor and the product that deposited slowly was collected after three days, washed with 2-propanol and then ether (Crop 4).

The (+)BCS complex (Crops 1-3) was converted to the tetrachlorozincate(II) salt by dissolving in 6 F HCl (0.1 g/10 ml) at 40° and then adding $ZnCl_2$ (2.5 g/0.1 g). The product that was slowly deposited was collected after 24 hours, washed with 2-propanol and then ether.

All crops were recrystallised to constant rotation. The results were:

Crop Number	Weight of $ZnCl_4^{2-}$ salt (g)	$[M]_{517}$ (deg.dm^{-1}.$\underline{M}^{-1}$.$100cm^3$)
1	0.087	+1992
2	0.093	+ 2545
3	0.031	+2206
4	0.077	-2392

A solution $(-)_{589}$-D-Co(pn)(dien)Cl^{2+} (assumed optically pure) in 0.1 F $HClO_4$ has $[M]_{595}$ = -612.5, $[M]_{571}$ = 0, $[M]_{517}$ = +2545, $[M]_{443}$ = 0, $[M]_{425}$ = -241.6, $[M]_{400}$ = 0, $[M]_{380}$ = +101.1.

A solution of 94.0% optically pure (based on the (-) isomer) in 0.1 F $HClO_4$ has $[M]_{595}$ = +569.9, $[M]_{571}$ = 0, $[M]_{517}$ = -23 92,[M]$_{443}$ = 0, $[M]_{425}$ = +228.5, $[M]_{400}$ = 0, $[M]_{380}$ = -62.1.

Table 2.8

Analytical Data for [Co(pn)(dien)X]Y

Complex	Calculated					Found				
	C%	H%	N%	Co%	X%[a]	C%	H%	N%	Co%	X%[a]
$[Co_2(pn)_2(dien)_2O_2](ClO_4)_4.H_2O$	18.27	5.26	15.22	12.81		18.52	5.25	14.61	12.92	
$[Co(pn)(dien)Cl]ZnCl_4$ - A	17.56	4.84	14.63	12.31	37.05	17.68	4.80	14.41	12.25	37.11
- B						17.48	4.73	14.66	12.27	36.95
- G						17.21	4.98		12.14	36.95
$[Co(pn)(dien)Cl]ZnCl_4.3/2H_2O$ - C	16.62	5.18		11.65	35.04	16.70	5.32		11.42	35.00
- D						16.65	5.17		11.48	34.95
$[Co(pn)(dien)Cl]ZnCl_4.2H_2O$ - H	16.33	5.28		11.45	34.43	16.51	5.25		11.50	34.10
- I						15.98	5.28		11.41	34.52
$[Co(pn)(dien)Cl]ZnBr_4$ - A				8.97	54.07				8.85	54.10
- B									8.95	54.05
- G									8.92	54.10
$[Co(pn)(dien)Cl]ZnBr_4.3/2H_2O$ - C				8.62	51.93				8.50	51.82
- D									8.56	51.85

Table 2.8 (contd.)

Complex	Calculated					Found				
	C%	H%	N%	Co%	X%[a]	C%	H%	N%	Co%	X%[a]
$[Co(pn)(dien)Cl]ZnBr_4.2H_2O$ - H				8.51	51.26				8.40	51.30
$[Co(pn)(dien)\ Cl]CdBr_4$ - B				8.38	50.40				8.30	50.40
- G									8.41	50.35
- H									8.33	50.42
$[Co(pn)(dien)Cl]Zn(NCS)_4$ - A				10.35	47.04				10.21	46.83
- B									10.25	47.12
- D									10.26	47.15
- G									10.32	47.00
- H									10.30	47.10
$[Co(pn)(dien)Cl](ClO_4)_2$ - A	17.87	4.93		12.52	7.53	18.00	5.06		12.41	7.59
- B						17.73	5.14		12.43	7.44
- G						17.81	4.85		12.42	7.61
$[Co(pn)(dien)Br]ZnBr_4$ - A	11.99	3.31		8.41	56.98	12.12	3.30		8.35	57.25
- B						12.29	3.38		8.45	56.90
- G						12.25	3.36		8.30	56.92

Table 2.8 (contd.)

Complex	Calculated					Found				
	C%	H%	N%	Co%	X%[a]	C%	H%	N%	Co%	X%[a]
$[Co(pn)(dien)Br]ZnBr_4.2H_2O$ - I	11.44	3.43		8.02	54.35	11.71	3.42		8.15	54.50
- H						11.75	3.48		8.09	54.30
$[Co(pn)(dien)Br]CdBr_4$ - A				7.88	53.40				7.82	53.35
- B									7.80	53.35
$[Co(pn)(dien)Br]CdBr_4.3/2H_2O$ - D	10.86	3.39		7.61	51.60	11.33	3.37		7.75	51.32
$[Co(pn)(dien)Br]CdBr_4.2H_2O$ - H				7.53	51.01				7.49	51.00
$[Co(pn)(dien)Br]ZnCl_4$ - B				11.26	42.36				11.20	42.25
$[Co(pn)(dien)I]ZnCl_4$ - G	14.74	4.06		10.33	47.11	14.75	4.10		10.25	46.95
$[Co(pn)(dien)I]ZnCl_4.H_2O$ - H	13.86	4.49		9.72	44.31	14.43	4.38		9.85	44.75
$[Co(pn)(dien)N_3]ZnCl_4$ - A	17.31	4.77		12.14	29.21	17.85	4.61		12.03	29.29
$[Co(pn)(dien)N_3]CdBr_4$ - G				8.30	45.00				8.25	45.10
- H									8.18	45.10
$[Co(pn)(dien)N_3]ZnBr_4$ - A				8.88	48.19				8.83	48.12
$[Co(pn)(dien)N_3]Zn(NCS)_4$ - A				10.23	41.01				10.28	41.22

Table 2.8 (contd.)

Complex	Calculated					Found				
	C%	H%	N%	Co%	X%[a]	C%	H%	N%	Co%	X%[a]
$[Co(pn)(dien)NO_2]ZnCl_4$ - A	17.18	4.74		12.04	28.98	16.99	4.65		12.15	29.10
- B						16.87	4.74		12.00	28.75
- G						17.36	4.76		11.95	28.80
- I						17.25	4.69		12.15	28.70
$[Co(pn)(dien)NO_2]ZnCl_4.H_2O$ - C	16.57	4.97		11.61	27.95	16.25	4.99		11.71	28.12
- D						16.35	4.86		11.65	28.08
- H						16.34	4.96		11.55	28.05
$[Co(pn)(dien)NO_2]Zn(NCS)_4$ - A				10.16	40.07				10.14	40.10
- B									10.11	40.02
- G									10.19	40.13
$[Co(pn)(dien)NCS]Zn(NCS)_4$ - A				9.95	49.08				10.02	49.25
- B									9.93	49.15
- D									9.91	49.15
- G									9.85	49.10
- H									10.05	49.10

[a] Total Halide or SCN^- found by Ag^+ titration

(3) Isobutylenediamine

Analytical data for the complexes are presented in Table 2.13. Infrared spectra of the chloro $ZnCl_4^{2-}$ salts in the region 4000-400 cm^{-1} are presented in Fig. 2.4 and 2.5.

μ-Peroxobis(isobutylenediamine)bis(diethylenetriamine) dicobalt(III) Perchlorate Dihydrate: An aqueous solution (200 ml) of isobutylenediamine (8.0 ml) and diethylene-triamine (11 ml) was added to a stirred solution of $Co(NO_3)_2.6H_2O$ (30 g) in water (400 ml). A rapid stream of O_2 gas was passed through the stirred, room temperature solution and $NaClO_4.H_2O$ (30 g) was added in portions over 10 min. After one hour, $NaClO_4.H_2O$ (90 g) was added slowly. The product that deposited was collected, washed with 2-propanol and then ether. The yield was 37 g or 71.8%.

A sample for analysis was prepared by dissolving 1 g of the crude material in the minimum volume (ca. 75 ml) of 0.1 F $HClO_4$ at 80°. Excess $NaClO_4.H_2O$ was added to the stirred solution and the brown crystalline product that deposited was collected, washed and dried as above. A 77% recovery was obtained.

Isomers of Chloro(isobutylenediamine)(diethylenetriamine) cobalt(III) Tetrachlorozincate(II):

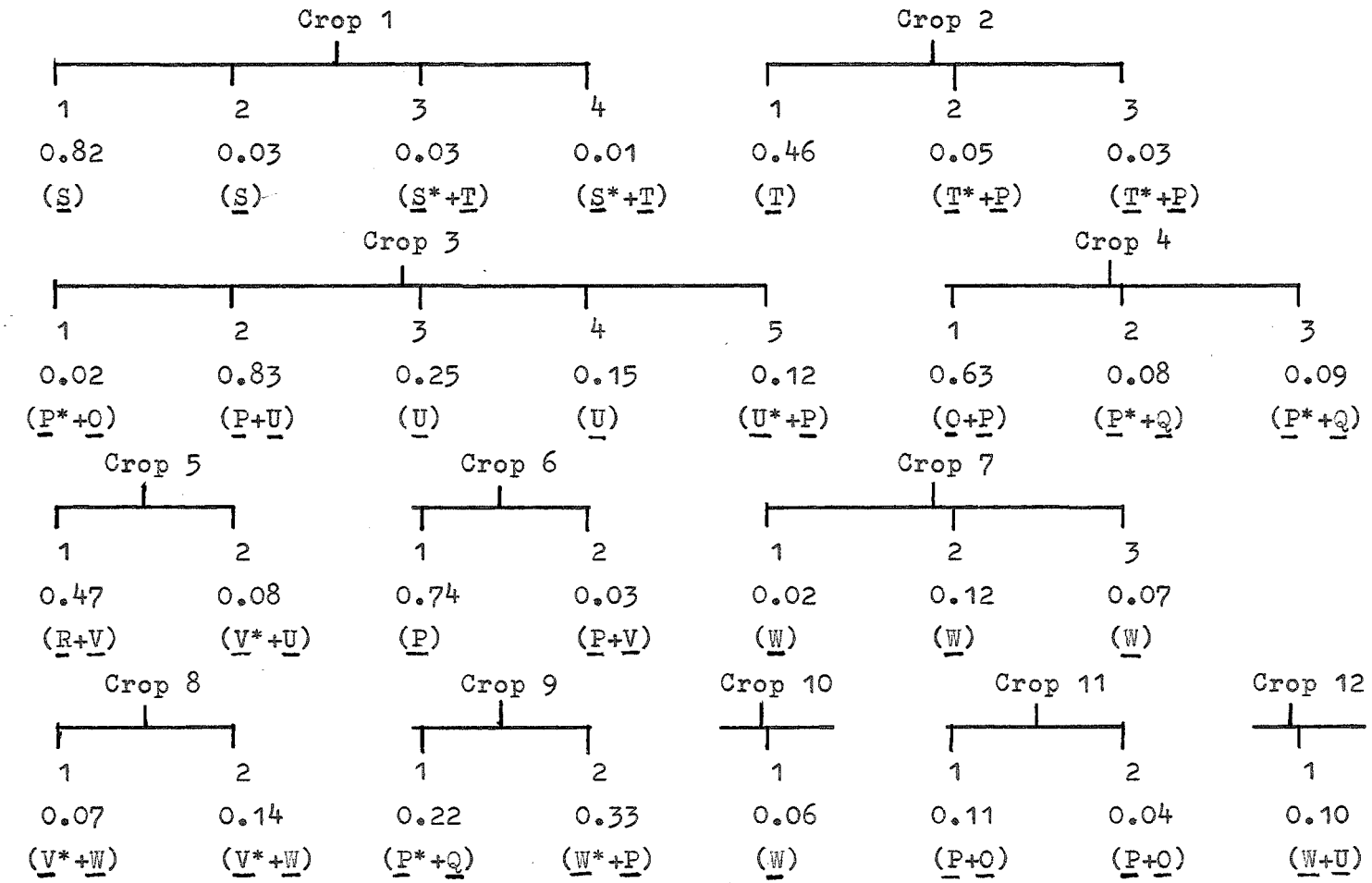
Method A: trans-$Co(dien)(NO_2)_3$ (14 g) was suspended in water (30 ml) and isobutylenediamine (4.5 ml, 100%) was added. The solution was stirred and allowed to digest the neutral complex on a steam bath at ca. 80°. After 30 min. the dark brown solution was cooled in ice and 12 F HCl (15 ml) containing $ZnCl_2$ (10 g) was slowly added. The solution was reheated for a further 1 hour during which time a crystalline product was deposited and it was collected in crops, washed with 2-propanol and then ether. The crude complex was recrystallised by dissolving each crop in 0.2 F CH_3CO_2H (1 g/20 ml) at 40° and then adding 12 F HCl (15 ml/1 g) containing $ZnCl_2$ (2.5 g/1 g). The purified product that was deposited on cooling to room temperature was collected in fractions and was washed and dried as above.

The aqueous mother liquor deposited further crops on slow evaporation at room temperature. These were recrystallised as above but using a corresponding reduction in the weights and volumes of the reagents used.

The total yield of chloropentaamine complex was 6.20 g or 26.9%. The isomeric composition of each fraction of recrystallised product is listed in Table 2.9.

Table 2.9

Isomeric Compositions of $[Co(ibn)(dien)Cl]ZnCl_4 \cdot xH_2O$; Method A



* denotes major component of fraction

Method B: trans-$Co(dien)(NO_2)_3$ (14 g) was suspended in water (30 ml) and isobutylenediamine (4.5 ml, 100%) was added. The mixture was heated on a steam bath (ca. 80°) until the neutral complex dissolved to give a dark brown solution. After cooling the solution in an ice bath, 12 F HCl (25 ml) was slowly added. The solution was reheated for a further 3 hours during which time a dark red colour formed. 12 F HCl (25 ml) containing $ZnCl_2$ (15 g) was then added and the crystalline product that deposited on cooling to room temperature was collected in crops, washed with 2-propanol and then ether. The crude product was recrystallised by dissolving it in 0.2 F CH_3CO_2H at 60° (50 ml/ 1 g) and then adding 12 F HCl (15 ml/1 g) containing $ZnCl_2$ (2.5 g/1 g). The purified product that deposited on cooling to room temperature was collected in fractions, washed and dried as above.

The aqueous mother liquor deposited further crops on slow evaporation at room temperature. These were recrystallised as above but using a corresponding reduction in the weights and volumes of the reagents used.

The total yield of chloropentaamine complex was 9.99 g or 43.4%. The isomeric composition of each fraction of recrystallised product is listed in Table 2.10.

Table 2.10

Isomeric Compositions of $[Co(ibn)(dien)Cl]ZnCl_4.xH_2O$; Method B

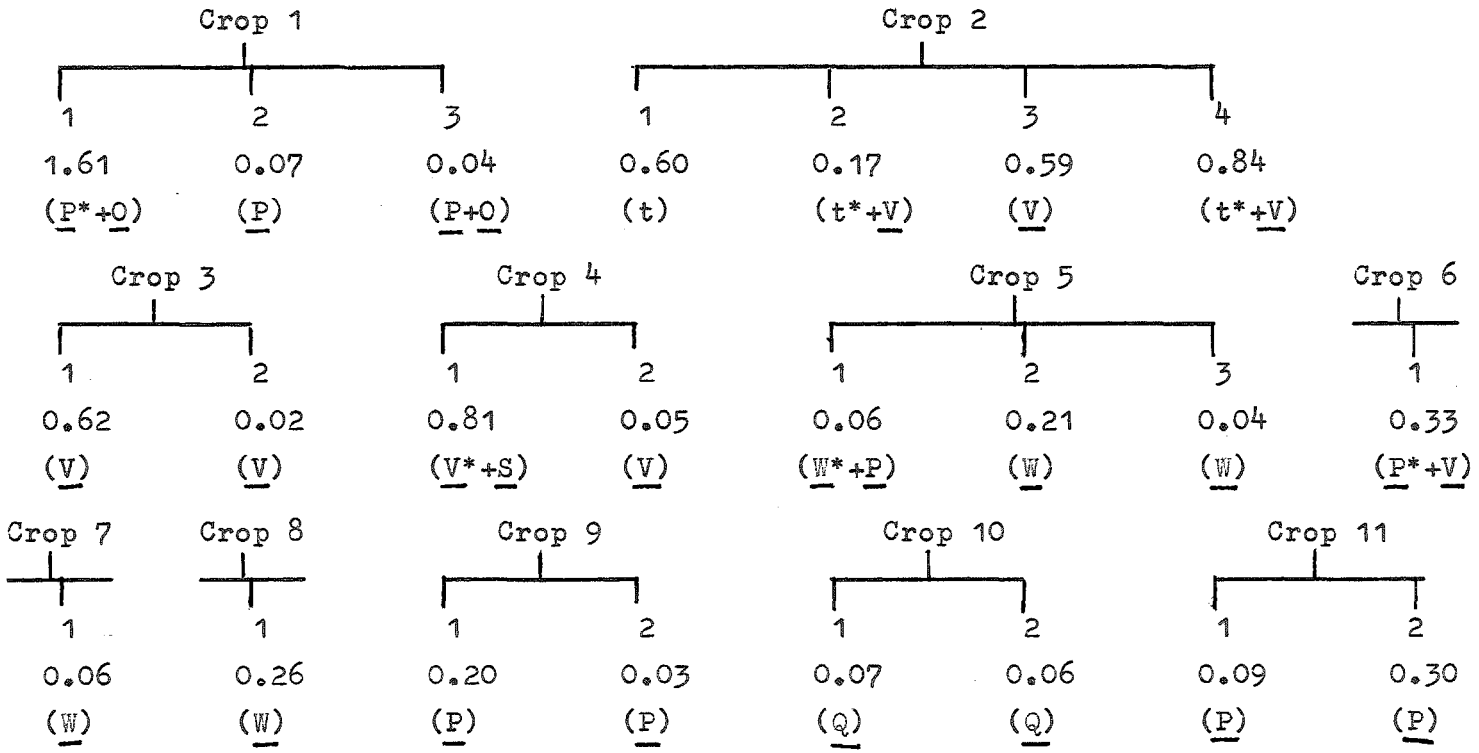
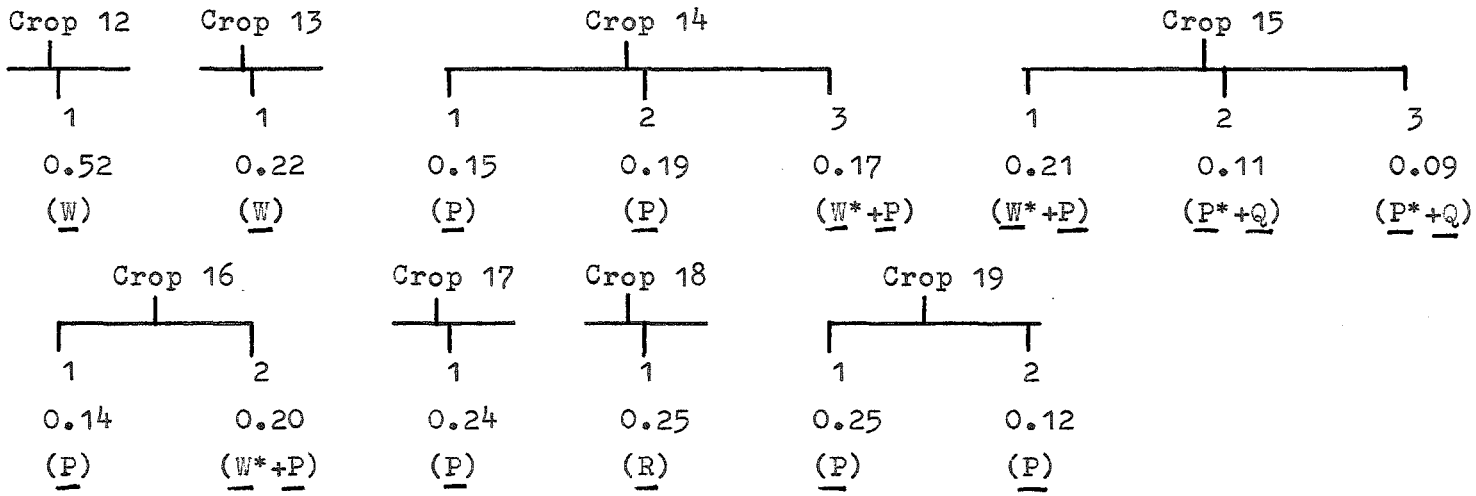


Table 2.10 (contd.)



* denotes major component of fraction

t trans - $[Co(ibn)_2Cl_2]Cl$

Method C: $[Co_2(ibn)_2(dien)_2O_2]ClO_4)_4.2H_2O$ (33.5 g) was added to a solution of 12 F HCl (90 ml) in water (170 ml). The solution was heated on a steam bath (ca. 80°) until the effervescence ceased (15 min.) and then $ZnCl_2$ (50 g) was added. The solution was reheated for a further 45 min. during which time a red crystalline material was deposited. This was collected from the hot solution, washed with 2-propanol and then ether. The crude product was recrystallised by dissolving it in 0.2 F CH_3CO_2H (1 g/20 ml) and then adding 12 F HCl (10 ml/1 g) containing $ZnCl_2$ (2.5 g/1 g). The purified product that deposited on cooling the solution to room temperature was collected in fractions and was washed and dried as above.

The aqueous mother liquor deposited further crops of crude product on slow evaporation at room temperature and these were recrystallised as above but using a corresponding reduction in the weights and volumes of the reagents used.

The total yield of chloropentaamine product was 13.93 g or 42.2%. The isomeric composition of each fraction of recrystallised product is listed in Table 2.11.

P and W-chloro(isobutylenediamine)(diethylenetriamine) cobalt(III) Tetrabromozincate(II): The P and W isomers of $[Co(ibn)(dien)Cl]ZnCl_4.xH_2O$ were separately dissolved in 0.2 F CH_3CO_2H at 40° (0.02 g/2 ml, 0.25 g/15 ml, respectively)

Table 2.11

Isomeric Composition of fractions of $[Co(ibn)(dien)Cl]ZnCl_4.xH_2O$; Method C

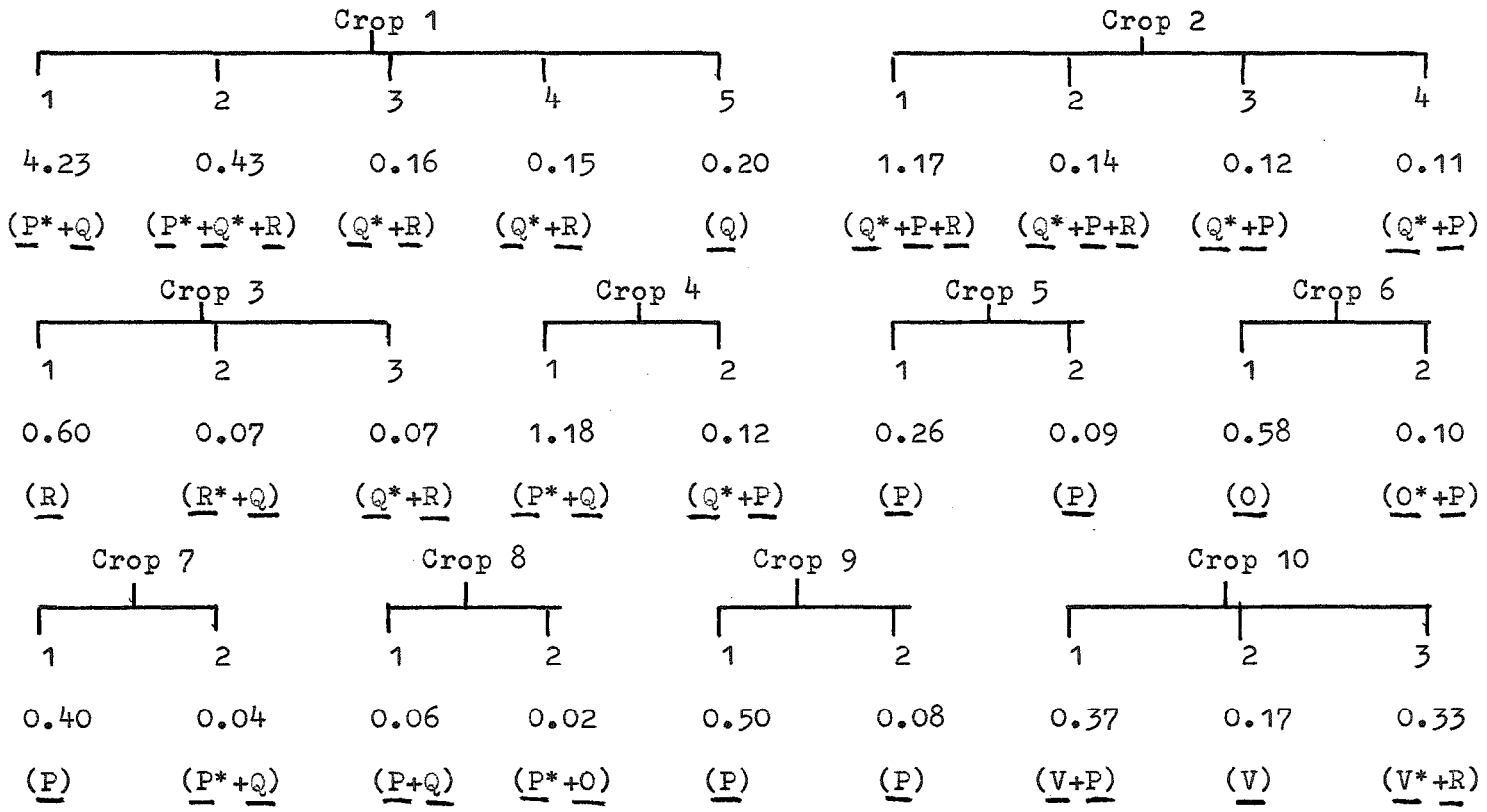
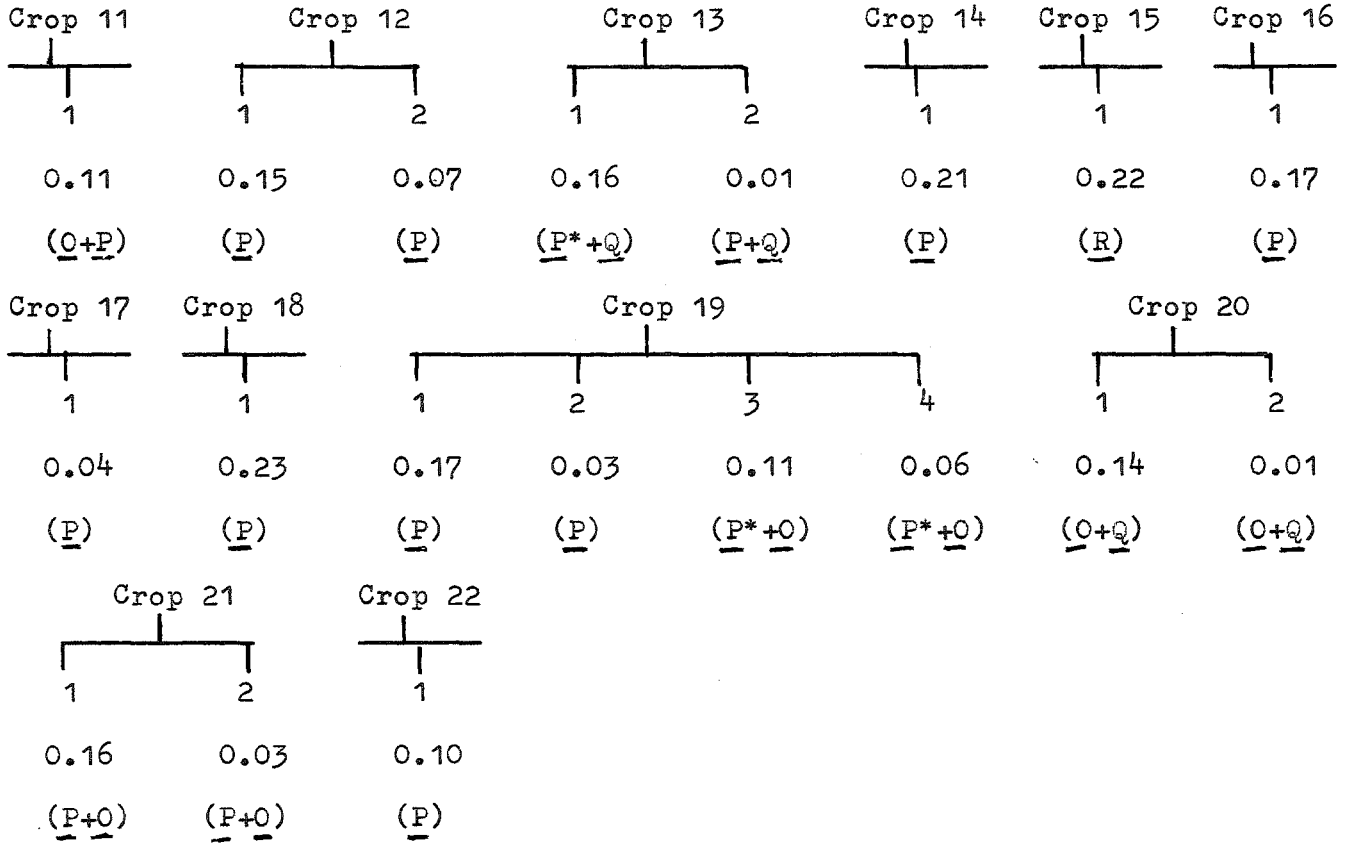


Table 2.11 (contd.)



* denotes major component(s) of fraction

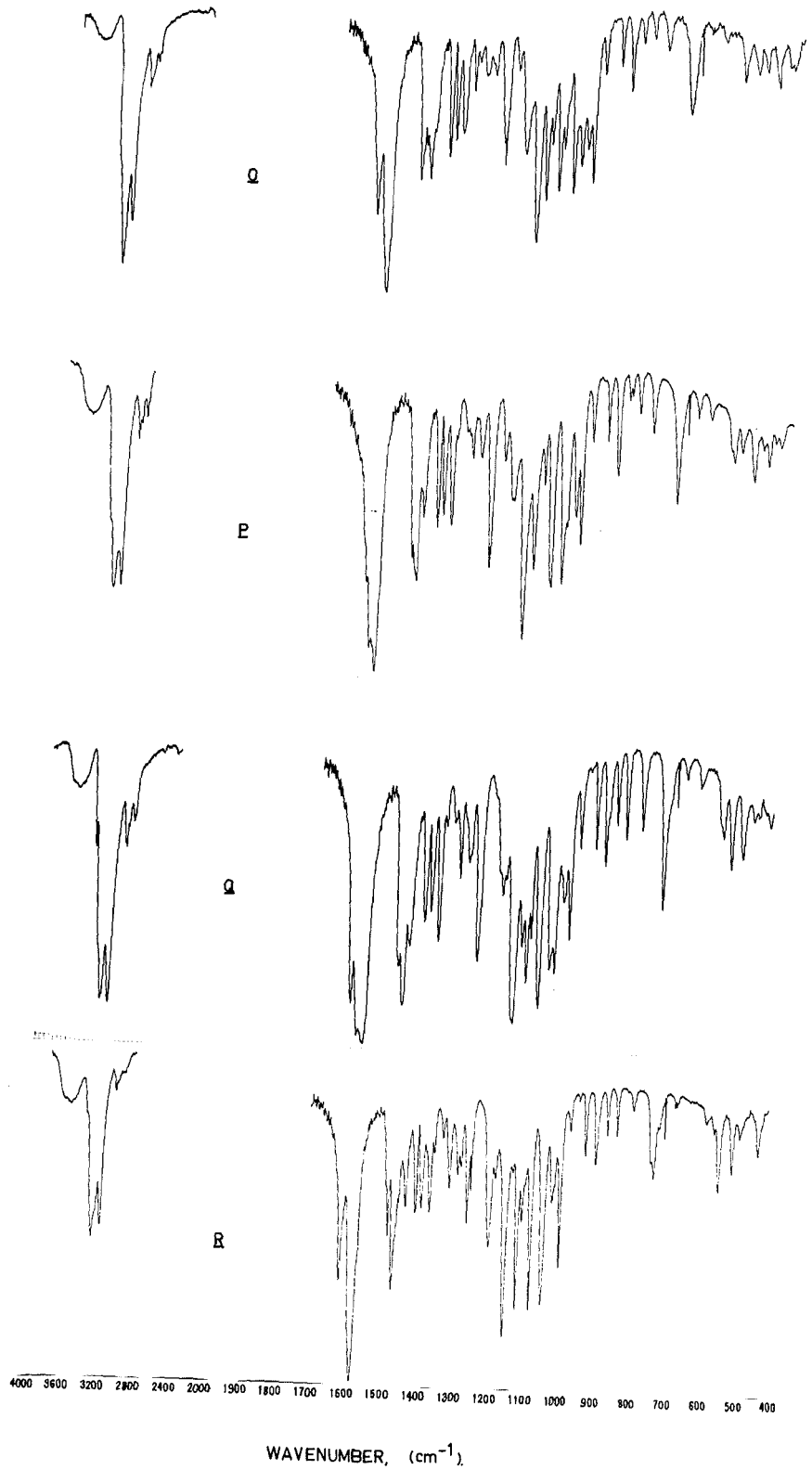
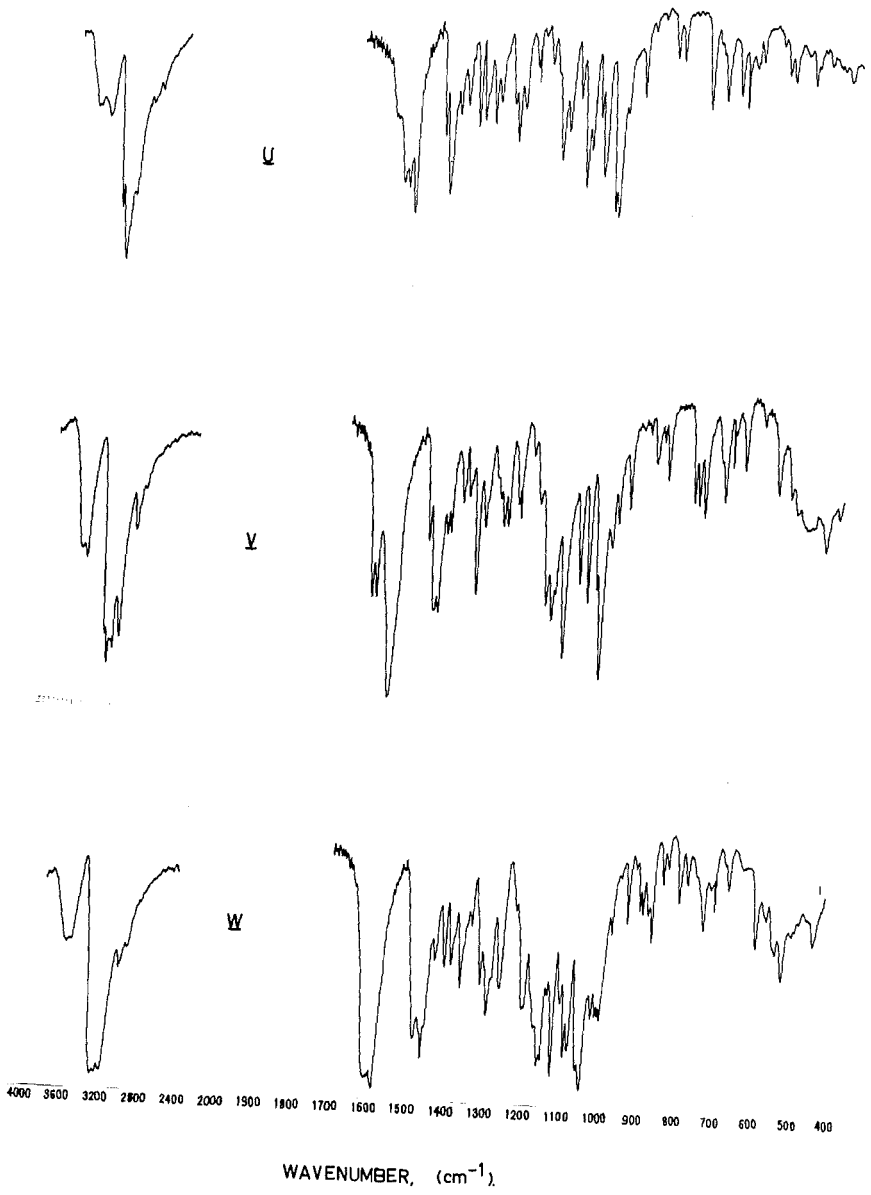


Figure 2.4 Infrared spectra of Q, P, Q and R - $[Co(ibn)(dien)Cl]ZnCl_4$ in the range 4000-400 cm^{-1} (KBr Disc).

Figure 2.5 Infrared spectra of U, V and W - $[Co(ibn)(dien)Cl]ZnCl_4 \cdot xH_2O$ in the range 4000-400 cm^{-1} (KBr Disc).



and a solution of 63% HBr (2 ml, 10 ml) containing $ZnBr_2$ (1 g, 2.5 g) was added. The products that deposited slowly on cooling the solutions in an ice bath were collected, washed with 2-propanol and then ether. The yields were P 51.2% and W 69.1%.

P-chloro(isobutylenediamine)(diethylenetriamine)cobalt(III) Tetrabromocadmiumate(II): P-$[Co(ibn)(dien)Cl]ZnCl_4$ (0.5 g) was dissolved in 0.2 F CH_3CO_2H (20 ml) at 40° and a solution of 63% HBr (15 ml) containing $CdBr_2.4H_2O$ (5 g) was added. The product that was immediately deposited was collected, washed with 2-propanol and then ether. The yield was 84.9%.

Q and R-bromo(isobutylenediamine)(diethylenetriamine) cobalt(III) Tetrabromozincate(II): $[Co_2(ibn)_2(dien)_2O_2](ClO_4)_4.2H_2O$ (3.5 g) was dissolved in water (15 ml) and 63% HBr (10 ml) was added. The solution was heated on a steam bath (ca. 80°) for 10 min. and then $ZnBr_2$ (5 g) was added. The crude product that was deposited immediately was collected in crops, washed with 2-propanol and then ether. The crude product was recrystallised by dissolving it in 0.2 F CH_3CO_2H (0.5 g/10 ml) at room temperature and then adding 63% HBr (5 ml/1 g) containing $ZnBr_2$ (2.5 g/1 g). The purified product that deposited immediately was collected in

fractions and was washed and dried as above. The total yield of bromopentaamine complex was 1.98 g or 40.5%. The isomeric composition of each fraction of recrystallised product is listed in Table 2.12. The Q and R isomers were separated from each other by refractionation of fractions containing high percentages of these isomers.

O, P, Q, R, U, V, W-Nitro(isobutylenediamine)(diethylene-triamine)cobalt(III) Tetrachlorozincate(II): The O, P, Q, R, U, V, W isomers of $[Co(ibn)(dien)Cl]ZnCl_4.xH_2O$ were separately dissolved in 0.2 F HCl (0.25 g/7.5 ml) and $NaNO_2$ (1 g) was added. The solutions were heated on a steam bath (ca. 80°) for (15 min., 15 min., 15 min., 15 min., 45 min., 45 min., 15 min.) during which time the mild effervescence ceased and the colour changed from red to orange. The hot solutions were slowly poured into 1:1 2-propanol/acetone (25 ml) containing 12 F HCl (1 ml) and $ZnCl_2$ (1.5 g). On cooling the solutions to room temperature the yellow products that were slowly deposited were collected, washed with acetone and then ether. The yields were O 69.0%, P 65.3%, Q 83.8%, R 85.8%, U 42.3%, V 36.4% and W 54.8%. The products derived from the P isomer contained a small quantity of the O isomer and similarly, those derived from the Q and R chloro isomers contain a mixture of the Q and R nitro isomers. Each nitro complex was separated by fractional crystallisation from 1:1 2-propanol/acetone.

Table 2.12

Isomeric Composition of $[Co(ibn)(dien)Br]ZnBr_4 \cdot xH_2O$

Crop 1		Crop 2		Crop 3		Crop 4
1	2	1	2	1	2	1
0.53	0.04	0.65	0.03	0.18	0.03	0.52
(Q*+R)	(Q+R)	(Q*+R)	(Q+R)	(R*+Q)	(R+Q)	(Q*+R)

* denotes major component of fraction

Qualitative Isomerisation Reactions

Small quantities of the pure isomers were taken and subjected to the following chemical reactions. The isomeric composition of the chloro $ZnCl_4^{2-}$ and nitro $ZnCl_4^{2-}$ salts was determined by examination of the infrared spectrum.

(a) Reaction with Nitrous Acid

Nitro compounds derived from the O, P, Q, R, "S", "T", U, V and W isomers of $[Co(ibn)(dien)Cl]ZnCl_4.xH_2O$ were prepared by the method described above. The products were decomposed by heating a solution of each in 3 F HCl on a steam bath (ca. 80°) for 1 hour. The $ZnCl_4^{2-}$ salts of the chloro isomers generated in this manner were deposited by the addition of $ZnCl_2$. The transformations that resulted were: O → O; P → P+O; Q → Q+R; R → Q+R; "S" → O; "T" → P+O; U → U; V → V; W → W.

(b) Base Hydrolysis

The O, P, Q, R, "S", "T", U, V and W isomers of $[Co(ibn)(dien)Cl]ZnCl_4.xH_2O$ were separately dissolved in water (0.25 g/10 ml) and 1 F NaOH (10 ml) was added. The solutions were heated at 50° for 10 min. and then 12 F HCl (10 ml) containing $ZnCl_2$ (4 g) was added. The solutions were left to stand at room temperature overnight and the product was collected, washed with 2-propanol and then ether. The results were O → P+O; P → P+O; Q → Q+R; R → Q+R; "S" → P+O; "T" → P+O; U → P+O; V → Q+R; W → W+P.

Table 2.13

Analytical Data for $[Co(ibn)(dien)X]Y.xH_2O$

Complex	Calculated				Found			
	C%	H%	Co%	X%[a]	C%	H%	Co%	X%[a]
$[Co(ibn)(dien)Cl]ZnCl_4$ - O	19.49	5.11	11.96	35.97	19.44	5.20	11.92	36.05
- P					19.48	5.13	11.91	35.92
- Q					19.47	5.14	11.90	35.63
- R					19.56	5.11	11.89	35.78
$[Co(ibn)(dien)Cl]ZnCl_4.3/2H_2O$ - W	18.48	5.43	11.34	34.10	18.46	5.49	11.40	34.05
$[Co(ibn)(dien)Cl]ZnCl_4.2H_2O$ - U	18.17	5.49	11.14	33.52	18.21	5.51	11.12	33.63
- V					18.16	5.49	11.15	33.57
$[Co(ibn)(dien)Cl]ZnBr_4$ - P			8.79	52.95			8.72	52.83
- W							8.79	53.01
$[Co(ibn)(dien)Cl]CdBr_4$ - P			8.21	49.47			8.25	49.53
$[Co(ibn)(dien)Br]ZnBr_4.H_2O$ - Q			8.04	54.49			8.12	54.75
- R							8.13	54.62

Table 2.13 (contd.)

Complex	Calculated				Found			
	C%	H%	Co%	X%[a]	C%	H%	Co%	X%[a]
$[Co(ibn)(dien)NO_2]ZnCl_4$ - O			11.71	28.17			11.65	28.22
- P							11.73	28.29
- Q							11.77	28.11
- R							11.69	28.30
- W							11.58	28.07
$[Co(ibn)(dien)NO_2]ZnCl_4.2H_2O$ - U			10.92	26.29			10.97	26.39
- V							10.83	26.32

[a] Total halide as found by Ag^+ titration

(4) N^1-isopropyl-2-methyl-1,2-propanediamine:

Analytical data for the complexes are presented in Table 2.16. Infrared spectra of the chloro $ZnCl_4^{2-}$ salts in the region 4000-400 cm^{-1} are presented in Fig. 2.6 and 2.7.

Isomers of chloro(N^1-isopropyl-2-methyl-1,2-propanediamine)(diethylenetriamine)cobalt(III) Tetrachlorozincate(II):

Method A: trans-$Co(dien)Cl_3$ (19.5 g) was suspended in water (50 ml) and N^1-isopropyl-2-methyl-1,2-propanediamine (8 ml, 100%) was added. The solution was heated on a steam bath (ca. 80°) for 30 min. and then it was cooled in an ice bath. 12 F HCl (60 ml) containing $ZnCl_2$ (25 g) was then slowly added. On standing the resultant orange-red solution at room temperature for 24 hours, the crude product commenced to crystallise and it was collected in crops, washed with 2-propanol and then ether. The crude product was recrystallised by dissolving it in 0.2 F CH_3CO_2H (1 g/30 ml) at 70° and then adding 12 F HCl (20 ml/1 g) containing $ZnCl_2$ (2.5 g/1 g). The purified product that deposited on cooling the solution to room temperature was collected in fractions, washed and dried as above.

Further crops of crude product were obtained on the slow evaporation of the aqueous mother liquor at room temperature. These were recrystallised as above but using a corresponding reduction in the weights and volumes of the reagents used.

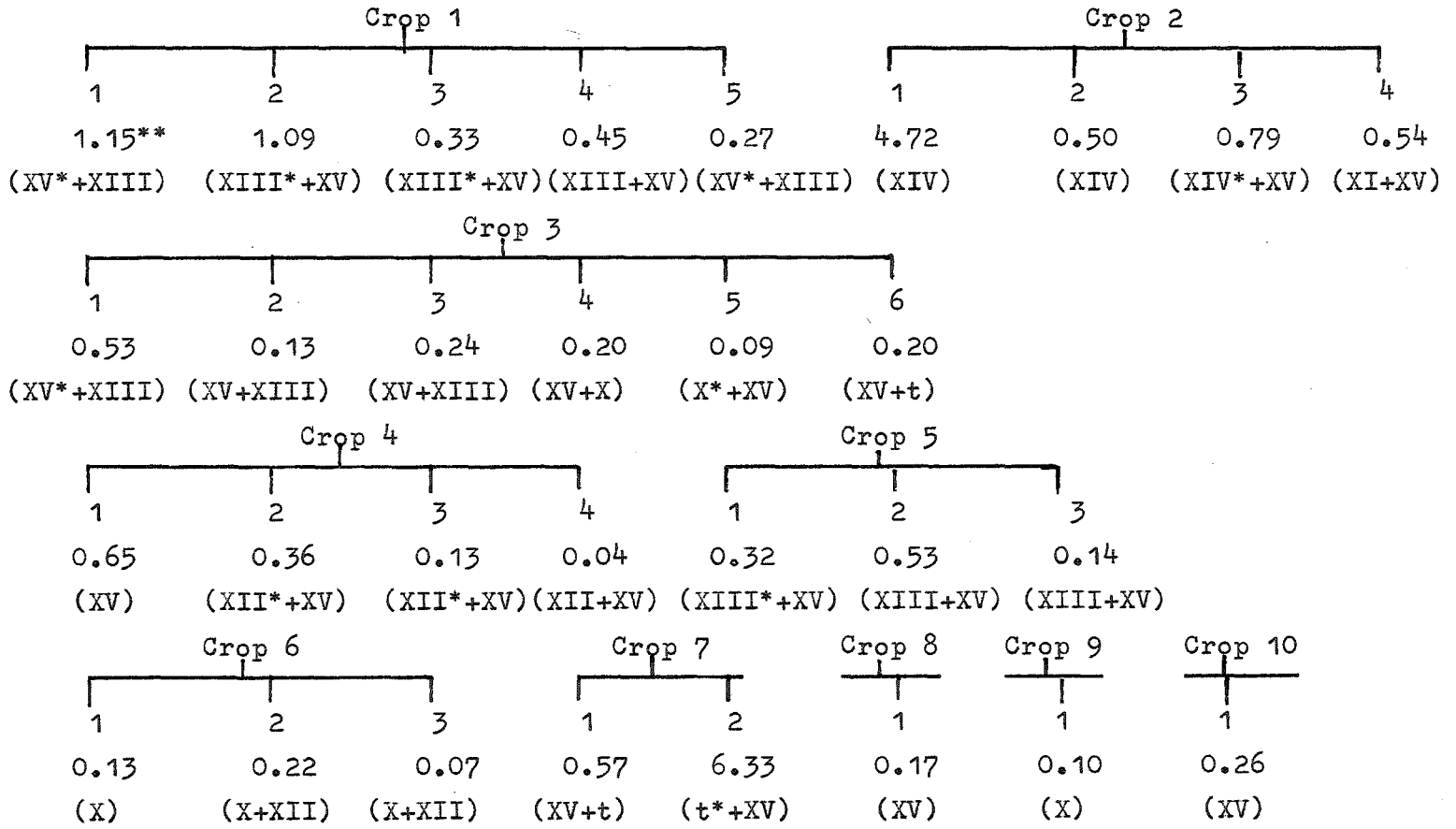
The total yield of chloropentaamine complex was 14.92 g or 38.4%. The isomeric composition of each fraction of recrystallised product is listed in Table 2.14.

Method B: trans-$Co(dien)(NO_2)_3$ (14 g) was suspended in water (30 ml) and N^1-isopropyl-2-methyl-1,2-propanediamine (4.0 ml, 100%) was added. The solution was heated on a steam bath (ca. 80°) for 1 hour and the neutral complex that remained was removed by filtration. 12 F HCl (20 ml) was slowly added to the ice cooled solution and the resulting solution was reheated for a further 3 hours. $ZnCl_2$ (10 g) was then added and the amine hydrochloride that deposited was removed by filtration. After three days at room temperature, the crude product commenced to crystallise and it was collected in crops, washed with 2-propanol and then ether. The crude product was recrystallised by dissolving it in 0.2 F CH_3CO_2H (0.2 g/10 ml) and then adding 12 F HCl (5 ml/0.2 g) containing $ZnCl_2$ (2 g/0.2 g). The purified product that deposited on cooling the solution to room temperature was collected, washed and dried as above.

The total yield of chloropentaamine complex was only 0.77 g or 3.1%. The isomer composition of each fraction of recrystallised product is listed in Table 2.15.

Table 2.14

Isomeric Compositions of Fractions of $[Co(Nip\text{-}ibn)(dien)Cl]ZnCl_4 \cdot xH_2O$; Method A

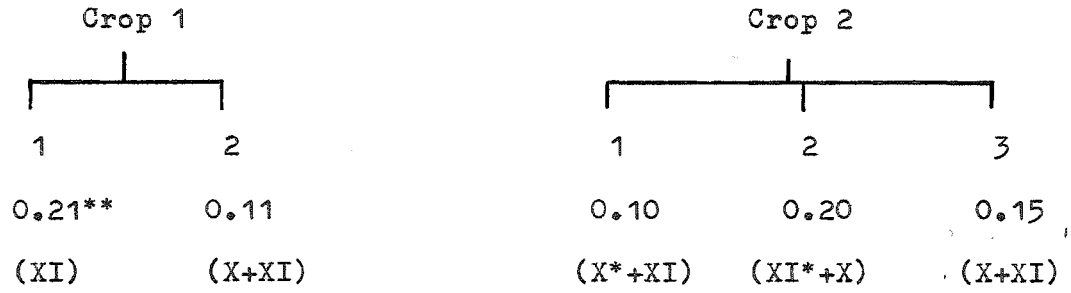


* denotes major component of fraction t = trans- $[Co(dien)(Nip\text{-}ibnH)Cl]Cl$

** weight in g

Table 2.15

Isomeric Compositions of fractions of $[Co(Nip\text{-}ibn)(dien)Cl]ZnCl_4 \cdot xH_2O$; Method B



* denotes major components of fraction

** weight in g

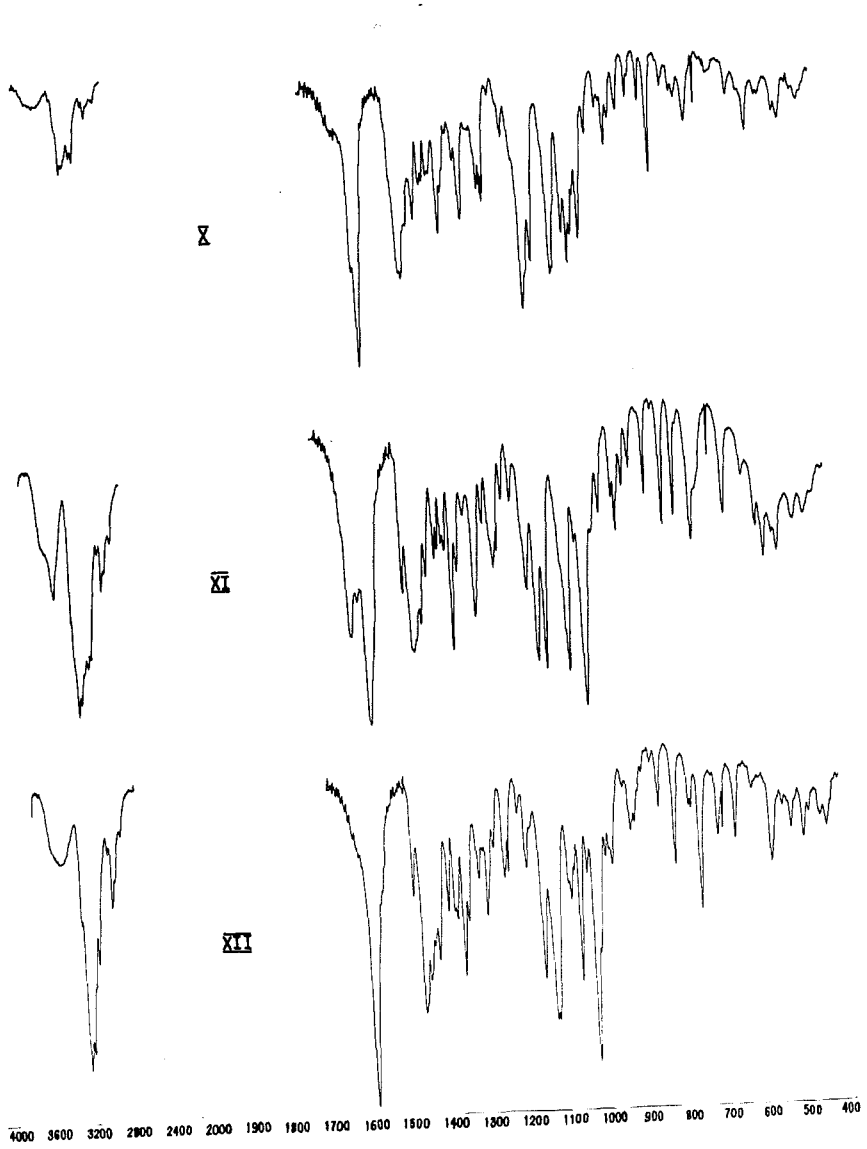


Figure 2.6 Infrared spectra of X, XI and XII - $[Co(Nip\text{-}ibn)(dien)Cl]ZnCl_4.xH_2O$ in the region 4000-400 cm^{-1} (KBr Disc).

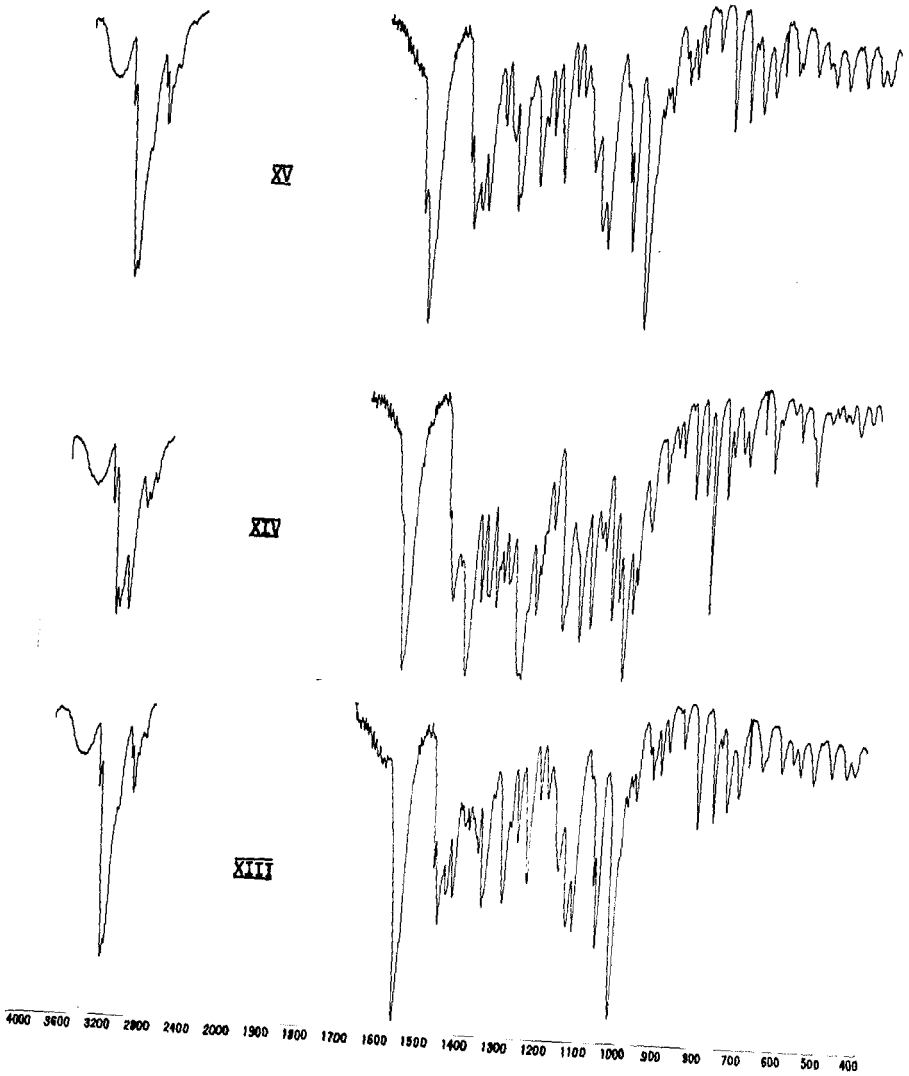


Figure 2.7 Infrared spectra of XIII, XIV and XV - [Co(Nip-ibn)(dien)Cl]ZnCl$_4$ in the region 4000-400 cm-1 (KBr Disc).

Qualitative Isomerisation Reaction - Base Hydrolysis

The X, XI, XII, XIII, "XIV" and XV isomers of $[Co(Nip\text{-}ibn)(dien)Cl]ZnCl_4.xH_2O$ were separately dissolved in water (0.25 g/5 ml) and 1 F NaOH (10 ml) was added. The solutions were allowed to stand at room temperature for 10 min. and then 12 F HCl (5 ml) containing $ZnCl_2$ (2.5 g) was added. The solutions were left to stand at room temperature overnight and the product that deposited was collected, washed with 2-propanol and then ether. The isomeric composition of the products was determined by examination of the infrared spectrum. The results were: X → X + XIII; XI → XII + XI; XII → XII + XI; XIII → X + XIII; "XIV" → "XIV" + XV; XV → XV.

Resolution of XI-$Co(Nip\text{-}ibn)(dien)Cl^{2+}$

XI-$[Co(Nip\text{-}ibn)(dien)Cl]ZnCl_4.H_2O$ (0.25 g) was dissolved in 0.2 F CH_3CO_2H at 40° (10 ml) and 5 drops glacial acetic acid was added. Ammonium (+)-α-bromo-camphor-π-sulphonate (0.25 g) was slowly added in 0.05 g positions. The pink precipitate that deposited after 15 min. was collected, washed with 2-propanol and then ether. On standing the solution at room temperature, a second crop of pink precipitate was obtained and this was collected, washed and dried as above. The (+)BCS salt was converted to the tetrachlorozincate(II) salts by dissolving each crop in 6 F HCl (0.1 g/5 ml) and then adding $ZnCl_2$ (1 g/0.1 g). The complex

obtained was collected, washed and dried as above (Crops 1 and 2).

12 F HCl (10 ml) containing $ZnCl_2$ (2.5 g) was added to the aqueous mother liquor and the product that deposited was collected from the ice cooled solution and was washed and dried as above (Crop 3).

All crops were recrystallised to constant rotation.

Crop Number	Weight of $ZnCl_4^{2-}$ Salt (g)	$[M]_{530}$*
1	0.073	- 80.1
2	0.062	-126.7
3	0.081	+113.2

*Units are $deg.dm^{-1}(M/100\ cm^3)^{-1}$

A solution of the fraction having maximum rotation of (+) -XI-Co(Nip-ibn)(dien)Cl^{2+} in 0.1 F $HClO_4$ has $[M]_{601}$ = +87.9, $[M]_{568}$ = 0, $[M]_{530}$ = -126.7, $[M]_{473}$ = 0, $[M]_{420}$ = +79.9, $[M]_{385}$ = +86.7, $[M]_{320}$ = 0.

A solution of the fraction having maximum rotation of (-) -XI-Co(Nip-ibn)(dien)Cl^{2+} in 0.1 F $HClO_4$ has $[M]_{601}$ = -78.2, $[M]_{568}$ = 0, $[M]_{530}$ = +113.2, $[M]_{473}$ = 0, $[M]_{420}$ = -71.1, $[M]_{385}$ = -77.0, $[M]_{320}$ = 0.

Table 2.16

Analytical Data for $[Co(Nip\text{-}ibn)(dien)Cl]ZnCl_4.xH_2O$

Complex	Calculated				Found			
	C%	H%	Co%	X%[a]	C%	H%	Co%	X%[a]
$[Co(Nip\text{-}ibn)(dien)Cl]ZnCl_4.H_2O$ - XI	23.89	6.01	10.66	32.06	23.97	5.91	10.59	32.12
$[Co(Nip\text{-}ibn)(dien)Cl]ZnCl_4$ - X	24.70	5.84	11.02	33.14	24.82	5.80	11.05	33.10
- XII					24.74	5.86	11.11	33.02
- XIII					24.99	6.06	11.13	33.22
- XV					25.28	6.17	11.08	33.15

[a] Total halide as found by Ag^+ titration

(5) Stilbenediamine

Analytical data for the complexes are presented in Table 2.18. Infrared spectra of the chloro $ZnCl_4^{2-}$ salts in the region 4000-400 cm^{-1} are presented in Fig. 2.8.

Isomers of Chloro(stilbenediamine)(diethylenetriamine) cobalt(III) Tetrachlorozincate(II): trans-$Co(dien)Cl_3$ (6 g) was suspended in methanol (400 ml) containing NaOH (1.5 g) and stilbenediamine (8 g) was added. The solution was boiled under reflux for 15 min. and then it was filtered. 12 F HCl (50 ml) was added to the red filtrate and the stilbenediamine dihydrochloride that deposited immediately was removed by filtration. $ZnCl_2$ (10 g) was then added to the orange-red filtrate and the solution was allowed to stand at room temperature. After 12 hours, the crystalline product that deposited was collected, washed with 2-propanol then ether. The crude material was recrystallised by dissolving it in methanol (1 g/50 ml) at 60° and then adding 12 F HCl (10 ml/1 g) containing $ZnCl_2$ (2.5 g/1 g). The purified product that deposited on cooling was collected in fractions and was washed and dried as above.

The mother liquor deposited further crops of crude product on slow evaporation at room temperature and these were recrystallised as above but using a corresponding reduction in the weights and volumes of the reagents used.

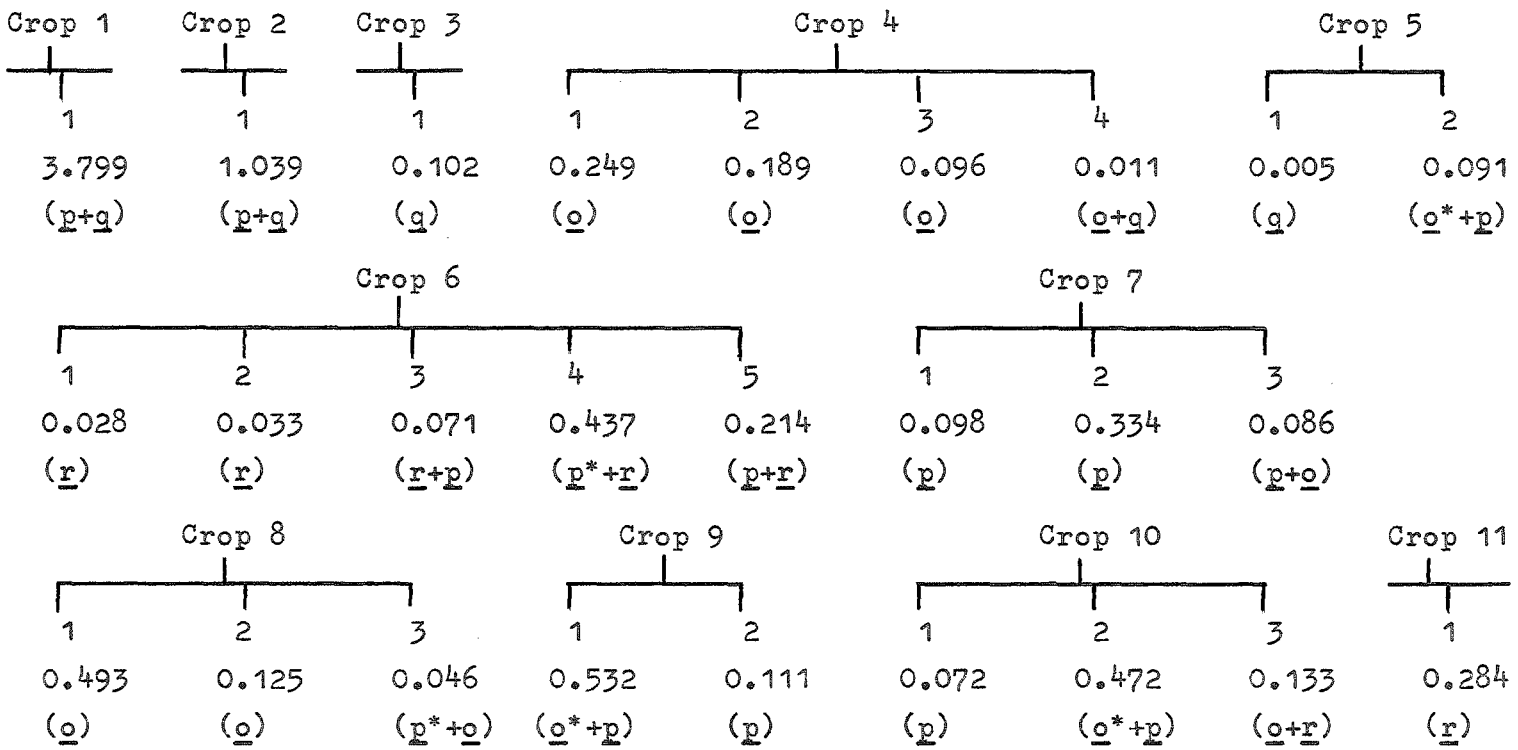
The total yield of chloropentaamine isomers was 9.150 g or 66.3%. The isomeric composition of each fraction of recrystallised product is listed in Table 2.17.

o-Bromo(stilbenediamine)(diethylenetriamine)cobalt(III) Tetrabromozincate(II): o-$[Co(stien)(dien)Cl]ZnCl_4$ (0.25 g) was dissolved in water (100 ml) at 60° and 50% HBr (15 ml) was added. The solution was boiled under reflux for 5 hours during which time part of the purple product was deposited. The hot suspension was poured into 50% HBr (20 ml) containing $ZnBr_2$ (2 g). After cooling to room temperature the purple product was collected, washed with 2-propanol and then ether. The yield was 58.4%.

p-Bromo(stilbenediamine)(diethylenetriamine)cobalt(III) Tetrabromocadmiumate(II): p-$[Co(stien)(dien)Cl]ZnCl_4$ (0.25 g) was suspended in methanol (30 ml) and 50% HBr (10 ml) was added. The solution was boiled under reflux (ca. 61-65°) for 3 hours. The hot solution was then poured into 50% HBr (10 ml) containing $CdBr_2.4H_2O$ (4 g). The purple product that slowly deposited on cooling to room temperature was collected, washed with 2-propanol and then ether. The yield was 65.4%. The same product was obtained when q-$[Co(stien)(dien)Cl]ZnCl_4$ was used as the starting material.

Table 2.17

Isomeric Compositions of fractions of $[Co(stien)(dien)Cl]ZnCl_4$



* denotes major component of fraction

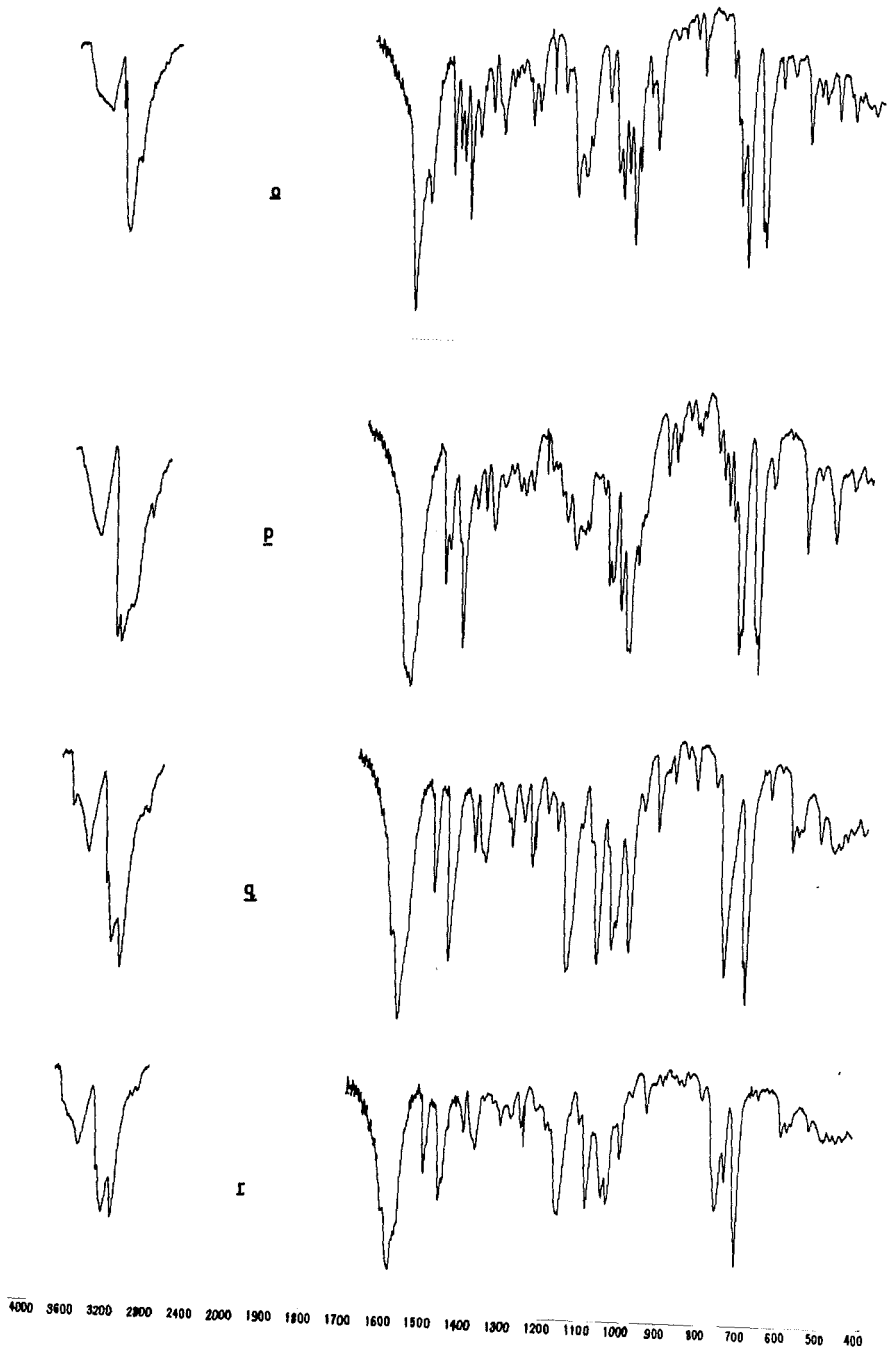


Figure 2.8 Infrared spectra of o, p, q and r - $[Co(stien)(dien)Cl]ZnCl_4$ in the region 4000-400 cm^{-1} (KBr Disc).

p-Nitro(stilbenediamine)(diethylenetriamine)cobalt(III) Tetrachlorozincate(II): p-[Co(stien)(dien)Cl]$ZnCl_4$ (1 g) was dissolved in 5% aqueous methanol (30 ml) and $NaNO_2$ (2 g) and 1 F HCl (3 ml) were added. The solution was heated on a steam bath (ca. 75°) for 20 min. during which time the mild effervescence ceased and the colour changed from red to orange. The hot solution was slowly poured into 1:1 2-propanol/acetone (100 ml) containing 12 F HCl (0.5 ml) and $ZnCl_2$ (4 g). On addition of water (100 ml) the yellow product that deposited was collected, washed with 2-propanol and then ether. The yield was 60.3%. The product is appreciably soluble in acetone.

Table 2.18

Analytical Data for [Co(stien)(dien)X]Y

Complex	Calculated				Found			
	C%	H%	Co%	X%[a]	C%	H%	Co%	X%[a]
$[Co(stien)(dien)Cl]ZnCl_4$ - o	35.04	4.74	9.55	28.73	34.53	4.79	9.58	28.69
- p					34.56	4.80	9.62	28.60
- q					34.61	4.77	9.65	28.57
- r					34.53	4.82	9.57	28.63
$[Co(stien)(dien)Br]ZnBr_4$ - o			7.02	47.60			7.09	47.41
$[Co(stien)(dien)Br]CdBr_4$ - p			6.65	45.08			6.72	45.13
$[Co(stien)(dien)NO_2]ZnCl_4$ - p			9.39	22.60			9.51	22.42

[a] Total halide as found by Ag^+ titration

(B) Complexes of 1,3-diamines with diethylenetriamine

(1) 1,3-propanediamine

Analytical data for the complexes are presented in Table 2.23. Infrared spectra of the chloro $ZnCl_4^{2-}$ salts in the region 4000-400 cm^{-1} are presented in Fig. 2.9 and 2.10.

μ-Peroxobis(1,3-diaminopropane)bis(diethylenetriamine) dicobalt(III) Perchlorate Dihydrate: An aqueous solution (200 ml) of 1,3-diaminopropane (7 g) and diethylenetriamine (10.5 g) was added to a stirred solution of $Co(NO_3)_2.6H_2O$ (30 g) in 400 ml of water. A rapid stream of O_2 gas was passed through the stirred, room temperature solution and after 15 min. three 30 g portions of $NaClO_4.H_2O$ were added. The solution was stirred for a further 45 min. and then the brown-grey product that deposited was collected, washed with 2-propanol and then ether. The yield was 40.6 g or 84.5%.

A sample for analysis was prepared by dissolving 2 g of the crude product in 125 ml of water at 60° and then adding 20 g $NaClO_4.H_2O$. The brown crystalline product that deposited was collected, washed and dried as above. A 71% recovery was obtained.

Isomers of Chloro(1,3-diaminopropane)(diethylenetriamine) cobalt(III) Tetrachlorozincate(II)

Method A: Crude $[Co_2(tmd)_2(dien)_2O_2](ClO_4)_4.2H_2O$ (30 g) was added to a solution of 12 F HCl (85 ml) in water (170 ml).

The solution was heated on a steam bath (ca. 80°) until the effervescence ceased (15 min.) and then $ZnCl_2$ (50 g) was added. The heating was continued for a further 30 min. during which time a red crystalline product deposited. This was collected in crops from the cooling solution and was washed with 2-propanol and then ether. Each crop of the crude product was recrystallised by dissolving it in the minimum volume of 0.2 F HCl (0.5 g/25 ml) and then adding 12 F HCl (10 ml/0.5 g) and $ZnCl_2$ (1.5 g/0.5 g). The purified product that deposited on cooling, was collected in fractions and washed and dried as above.

On further evaporation of the aqueous mother liquor at room temperature, further crops were slowly obtained and these were recrystallised as above but using a corresponding reduction in volumes and weights of the reagents used.

The total yield of chloropentaamine product was 15.12 g or 51.6%. Table 2.19 lists the isomeric composition of the products.

Method B: trans-$Co(dien)(NO_2)_3$ (14 g) was suspended in 30 ml of water and 1,3-diaminopropane (4.0 ml, 100%) was added. The mixture was heated on a steam bath for one hour during which time the neutral complex dissolved to give a dark brown solution. 15 ml of 12 F HCl was added cautiously to the solution and the heating at ca. 80° was continued for a further 1.5 hour in which time a purple-red solution was

Table 2.19

Isomeric Composition of fractions of $[Co(tmd)(dien)Cl]ZnCl_4$; Method A

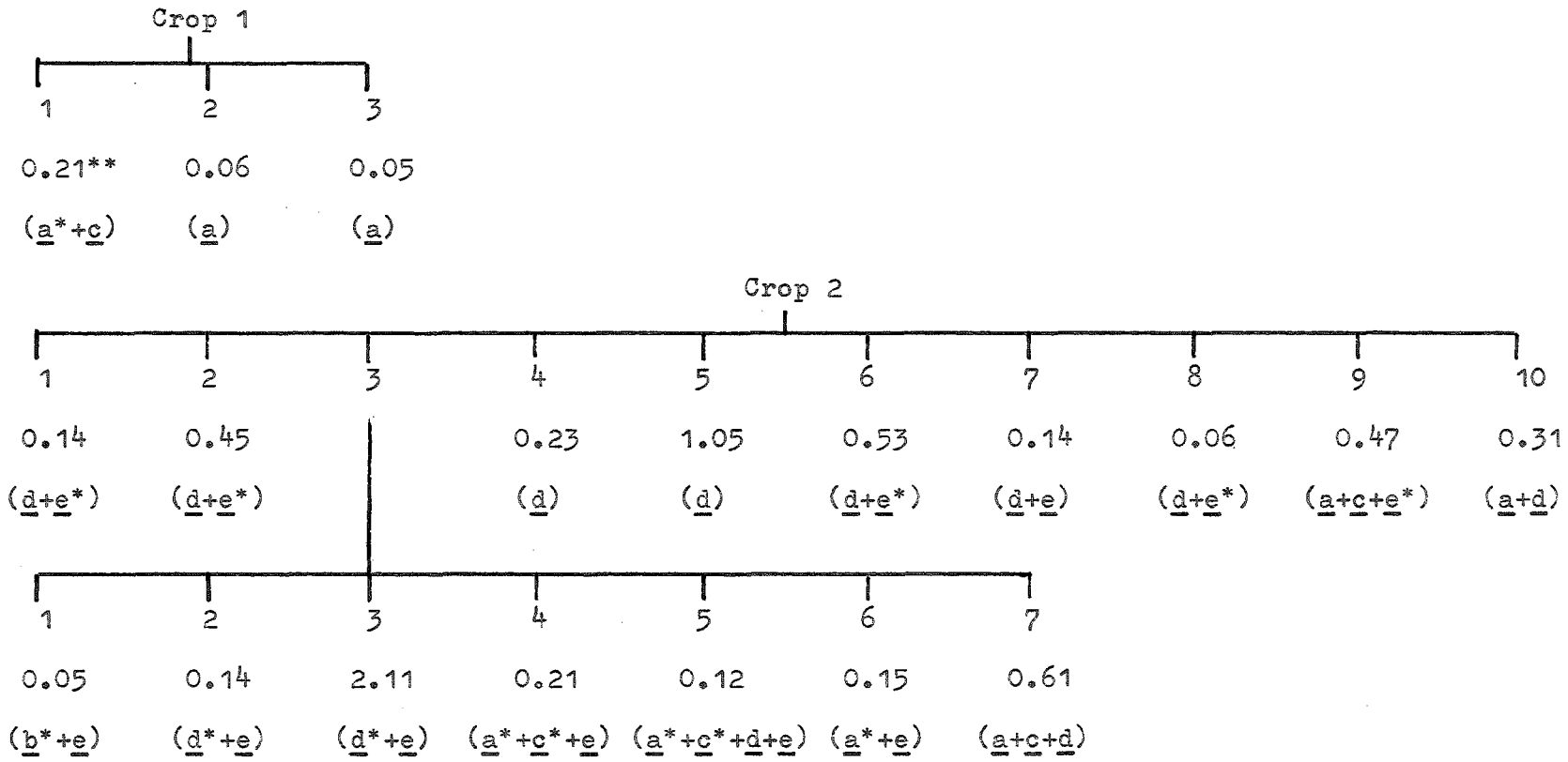
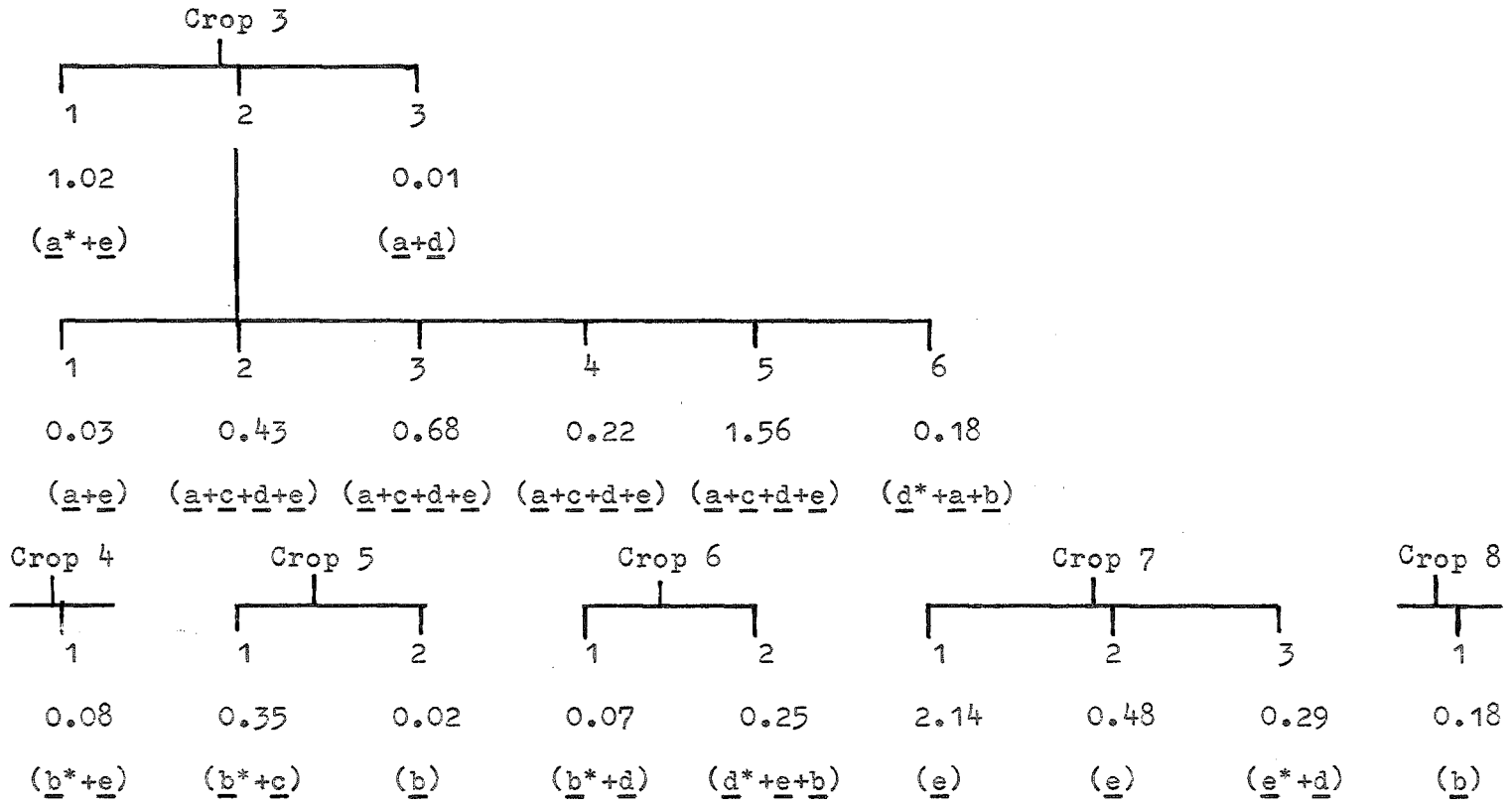


Table 2.19 (contd.)



* Indicates the major component(s) of the fraction

** weight in g

formed. 10 ml of 12 F HCl and 10 g of $ZnCl_2$ were added and the solution was allowed to cool to room temperature. The crude product that deposited was collected in crops and washed with 2-propanol and then ether.

Each crop of the crude product was recrystallised by dissolving it in 0.1 F HCl at 60° (1 g/15 ml) and then adding 12 F HCl (5 ml/1 g) and $ZnCl_2$ (2.5 g/1 g). The purified product that deposited on cooling, was collected in fractions and was washed and dried as above.

The total yield of chloropentaamine product was 14.21 g or 63.7%. Table 2.20 lists the isomeric composition of the products.

Method C: Method B was repeated on a double scale except that the 80° heating time (after the addition of 12 F HCl (30 ml)) was reduced to 45 min.

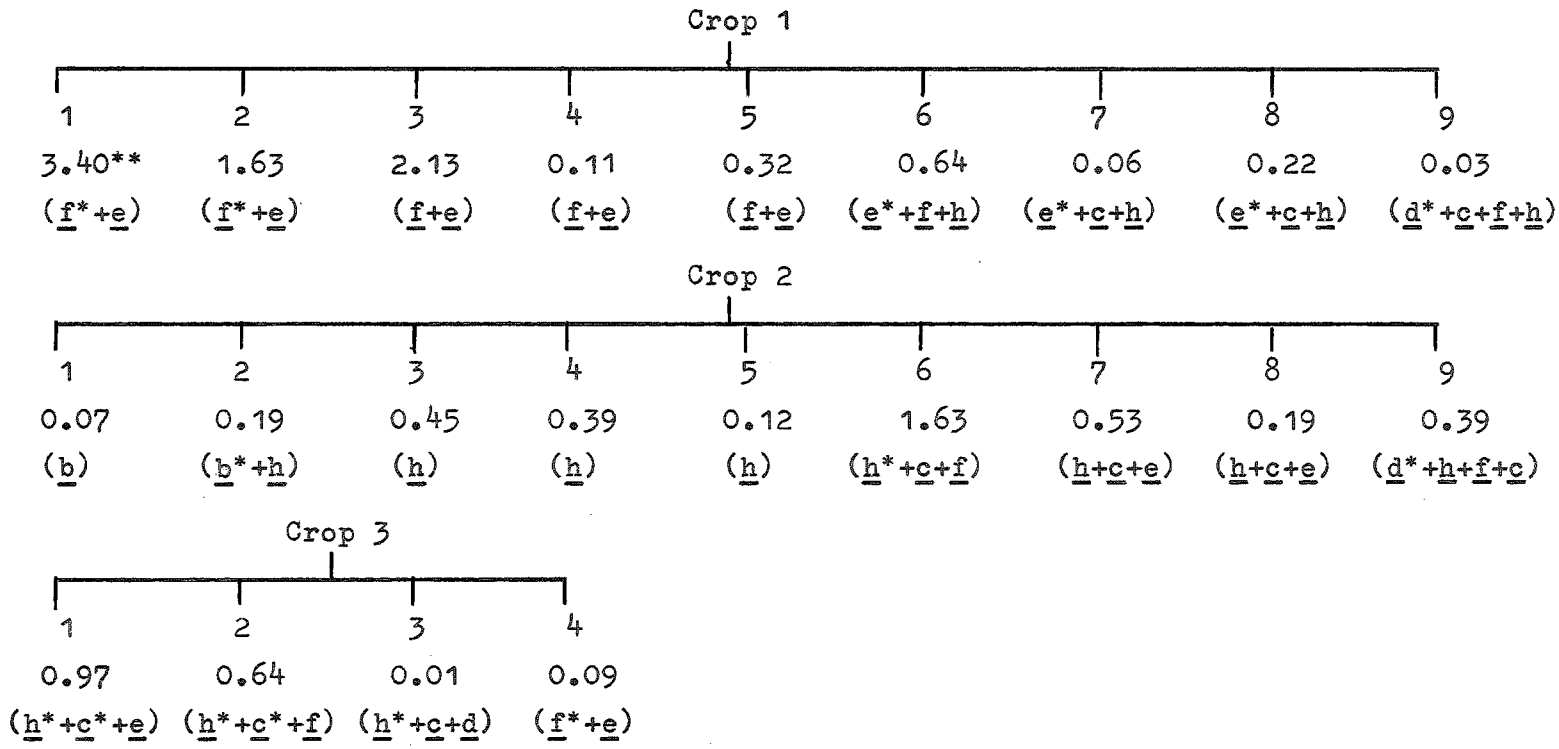
$ZnCl_2$ (15 g) and 12 F HCl (5 ml) were then added and the product that deposited on cooling was collected in crops, washed with 2-propanol and then ether. Each crop was recrystallised as in Method B.

On the slow evaporation of the aqueous mother liquor at room temperature, further crops were obtained and these were recrystallised as above but using a corresponding reduction in the weights and volumes of the reagents used.

The total yield of chloropentaamine product was 25.01 g or 56.2%. Table 2.21 lists the isomeric composition of the products.

Table 2.20

Isomeric Composition of $[Co(tmd)(dien)Cl]ZnCl_4$; Method B



* indicates the major component(s) of the fraction

** weight in g

Table 2.21

Isomeric Composition of $[Co(tmd)(dien)Cl]ZnCl_4$[≠]; Method C

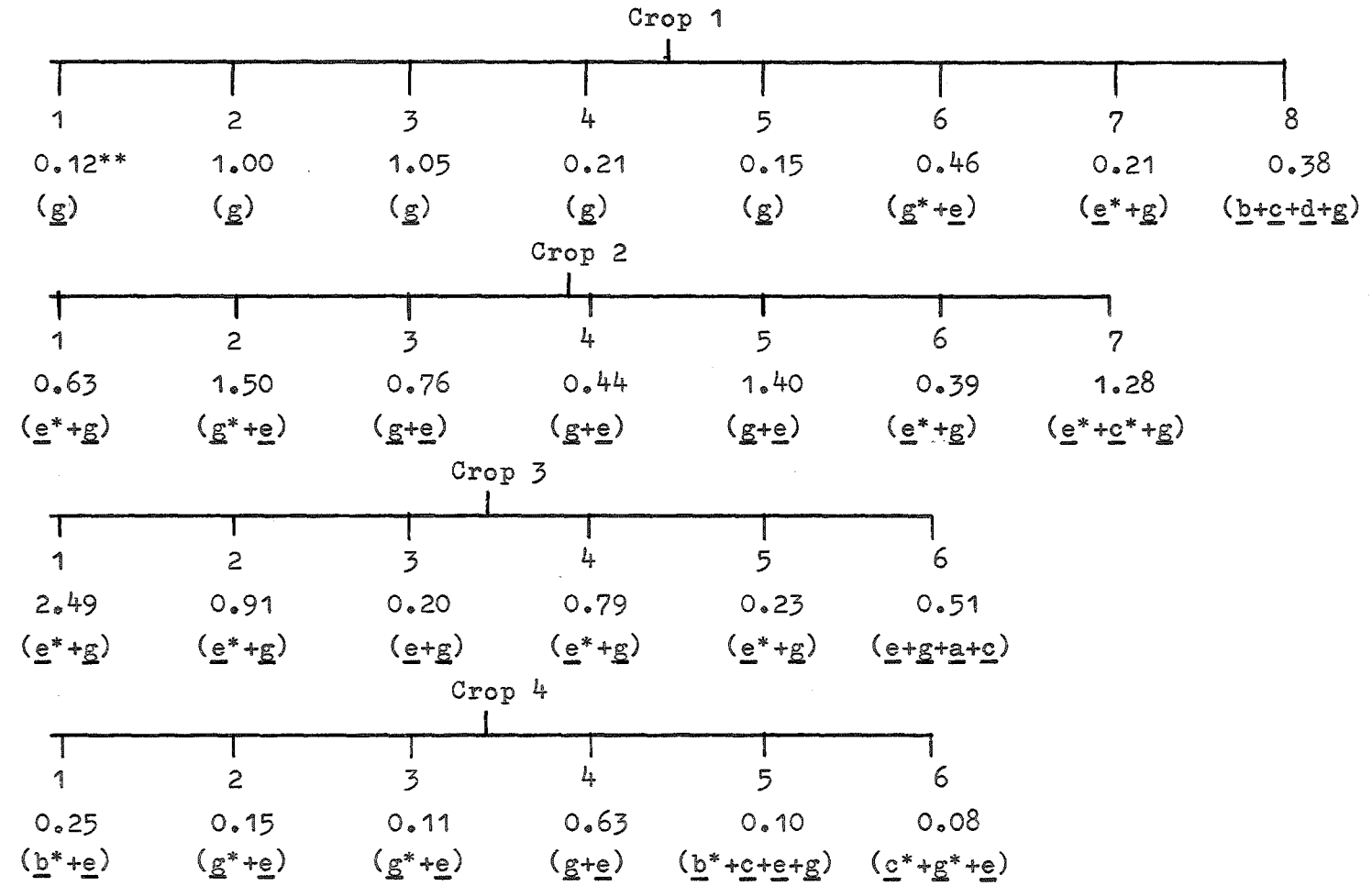
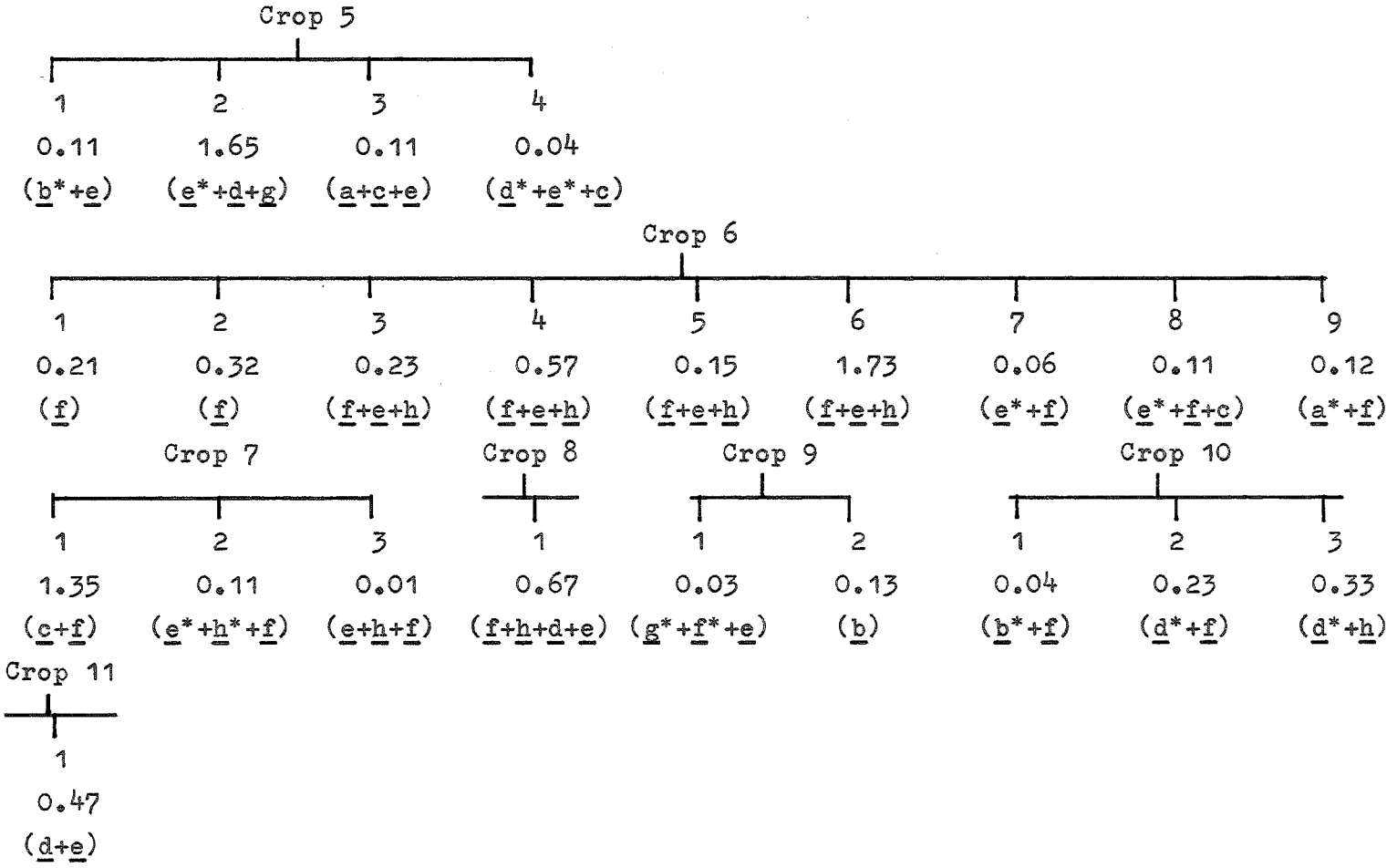


Table 2.21 (contd.)



≠ The "g-isomer" is shown to be a 3:1 f-[Co(tmd)(dien)Cl]$ZnCl_4$/ d-[Co(tmd)(dien)NO_2]$ZnCl_4$ mixture

* Indicates the major component(s) of the fraction

** Weight in g

Resolution of d-[Co(tmd)(dien)Cl]$ZnCl_4$

The pure isomer (4 g) was dissolved in water (15 ml) at 50° and glacial acetic acid (0.5 ml) was added. An equal weight of solid ammonium (+)-α-bromo-camphor-π-sulphonate was added slowly with stirring. The precipitate that began to deposit on cooling the solution to ca. 30° was collected in fractions (1-7). Each fraction was washed with 2-propanol and then ether. The α-bromo-camphor-π-sulphonate salt was converted to the tetrachlorozincate(II) salt by dissolving each fraction separately in 4 F HCl (0.5 g/10 ml) and then adding $ZnCl_2$ (1 g/0.5 g). The products (fractions 1-7) that deposited after 24 hours at room temperature were collected and washed and dried as above. The product from fraction 7 was recrystallised giving two crops, 7/1 and 7/2.

After two days at room temperature, the original mother liquor was treated with a solution of 12 F HCl (15 ml) containing $ZnCl_2$ (5 g). The product that deposited slowly, was collected in fractions (8-11) and washed and dried as above.

The molar rotations $[M]_\lambda$, of the $ZnCl_4^{2-}$ salt fractions, were determined at room temperature in 0.1 F $HClO_4$. The results were, in the order, Fraction number, (weight of $ZnCl_4^{2-}$ salt obtained in g), $[M]_{507}$[deg.dm^{-1}(moles/100cm^3)$^{-1}$]: 1, (0.002), +39.8; 2, (0.187), +40.0; 3, (0.035), +82.1; 4, (0.027), +99.2; 5, (0.051), +1435; 6, (0.024), +2039; 7/1, (0.113), +3926; 7/2, (0.050), +329.7. 8, (0.405), -211.8;

9, (0.351), -135.3; 10, (0.069), -323.6; 11, (0.275), -2481.

The fraction of $(-)_{589}$-d-Co(tmd)(dien)Cl^{2+} with the maximum rotation (crop 7/1) has the following molar rotations: $[M]_{602} = -1341$, $[M]_{566} = 0$, $[M]_{507} = +3926$, $[M]_{455} = 0$, $[M]_{430} = -943.4$, $[M]_{407} = +866.8$, $[M]_{356} = 0$.

The fraction of $(+)_{589}$-d-Co(tmd)(dien)Cl^{2+} with the maximum rotation (crop 11) (63.2% optically pure based on the $(-)_{589}$ form) has the following molar rotations: $[M]_{602} = +837.0$, $[M]_{566} = 0$, $[M]_{507} = -2481$, $[M]_{455} = 0$, $[M]_{430} = +588.9$, $[M]_{407} = +416.8$, $[M]_{377} = +866.8$, $[M]_{356} = 0$.

Separation of h Isomer

A sample containing ca. 30% or greater of the h isomer was found to be suitable.

$[Co(tmd)(dien)Cl]ZnCl_4$ (0.2 g) was dissolved in 0.2 F CH_3CO_2H (10 ml) at 50° and a solution of NaI (4 g) in water (10 ml) was added. On cooling to room temperature, the product that deposited was collected, washed with acetone and then ether. The crude product was converted to the tetrachlorozincate(II) salt by dissolving it in water (0.1 g/5 ml) and then adding 12 F HCl (5 ml) containing $ZnCl_2$ (2.5 g). The purple product (pure h isomer), deposited immediately, was collected, washed with acetone, 2-propanol and then ether.

Example of Isomerism with change in Anion

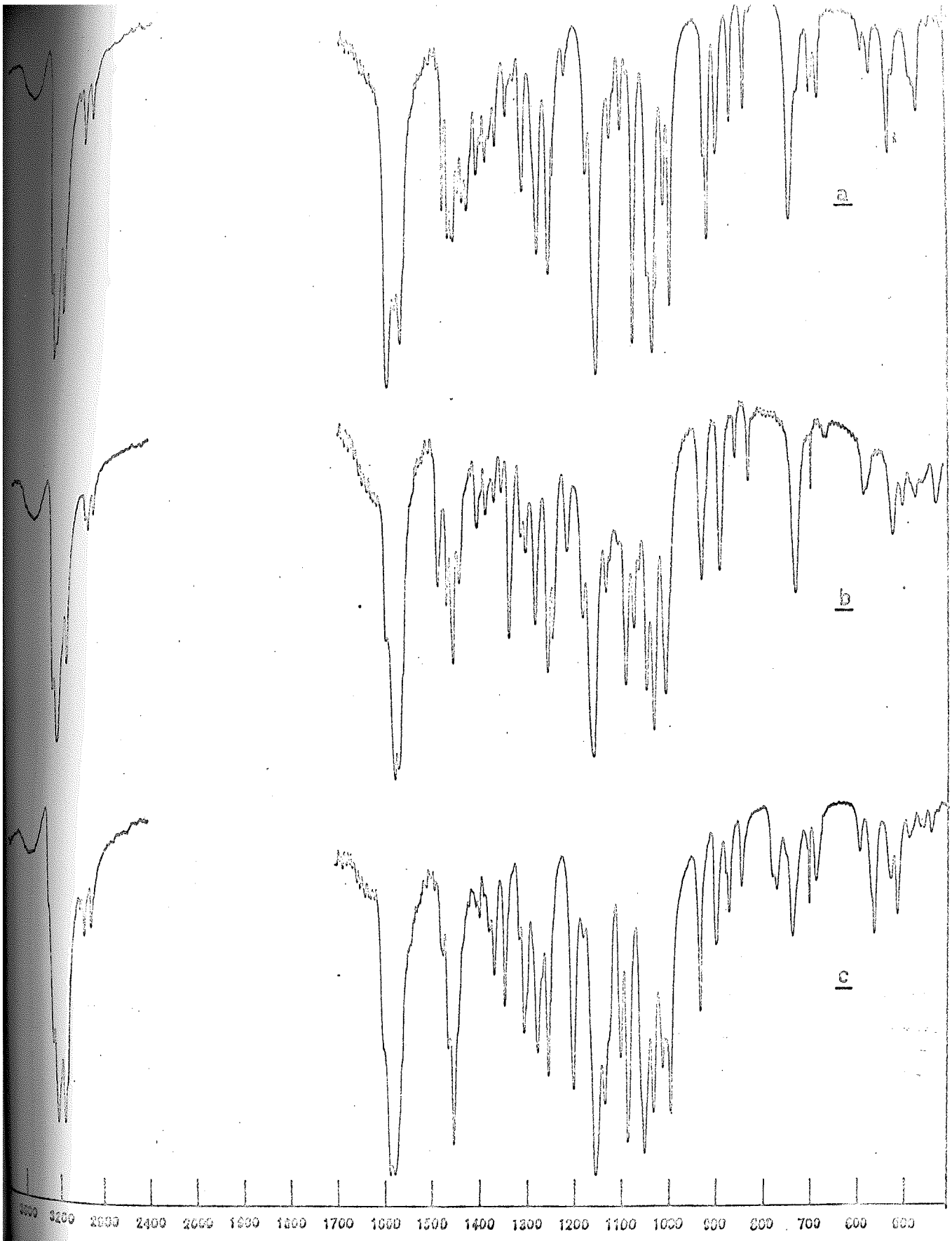
e or f-[Co(tmd)(dien)Cl]$ZnCl_4$ (0.5 g) were separately dissolved in room temperature 0.2 F CH_3CO_2H (15 ml) and 63% HBr (15 ml) containing $ZnBr_2$ (5 g) was added. The products that deposited on cooling to room temperature were collected in crops, washed with 2-propanol and then ether. The yields of d-[Co(tmd)(dien)Cl]$ZnBr_4$ were 75.6% (from f) and 74.2% (from e), respectively.

Qualitative Isomerisation Reactions

Small quantities of the pure isomers were taken and subjected to the following chemical reactions.

(a) Reflux in 6 F HCl: The pure isomers of [Co(tmd)(dien)Cl]$ZnCl_4$ were separately dissolved in 6 F HCl (0.25 g/12.5 ml) and the solutions were boiled under reflux for 30 min. 12 F HCl (5 ml) containing $ZnCl_2$ (2.5 g) was added and the products that deposited from the ice cooled solutions were collected, washed with 2-propanol and then ether. The results were: a → b+d+f, b → b+d, c → c, d → b+d, e → e+d+b, f → b+f+d, g → b+d+f, h → h.

(b) Base Hydrolysis (20-23°): The pure isomers of [Co(tmd)(dien)Cl]$ZnCl_4$ were separately dissolved in water (0.25 g/5 ml) and ca. 10 ml of 1 F NaOH was added until all the $Zn(OH)_2$ had precipitated. The red-orange solutions were allowed to stand at room temperature for 30 min. and then 12 F HCl (15 ml) and $ZnCl_2$ (4 g) were added. The solutions



ure 2.9 Infrared spectra of a, b and c - [Co(tmd)(dien)Cl] $ZnCl_4 . xH_2O$ the range 4000-400 cm^{-1} (KBr Disc).

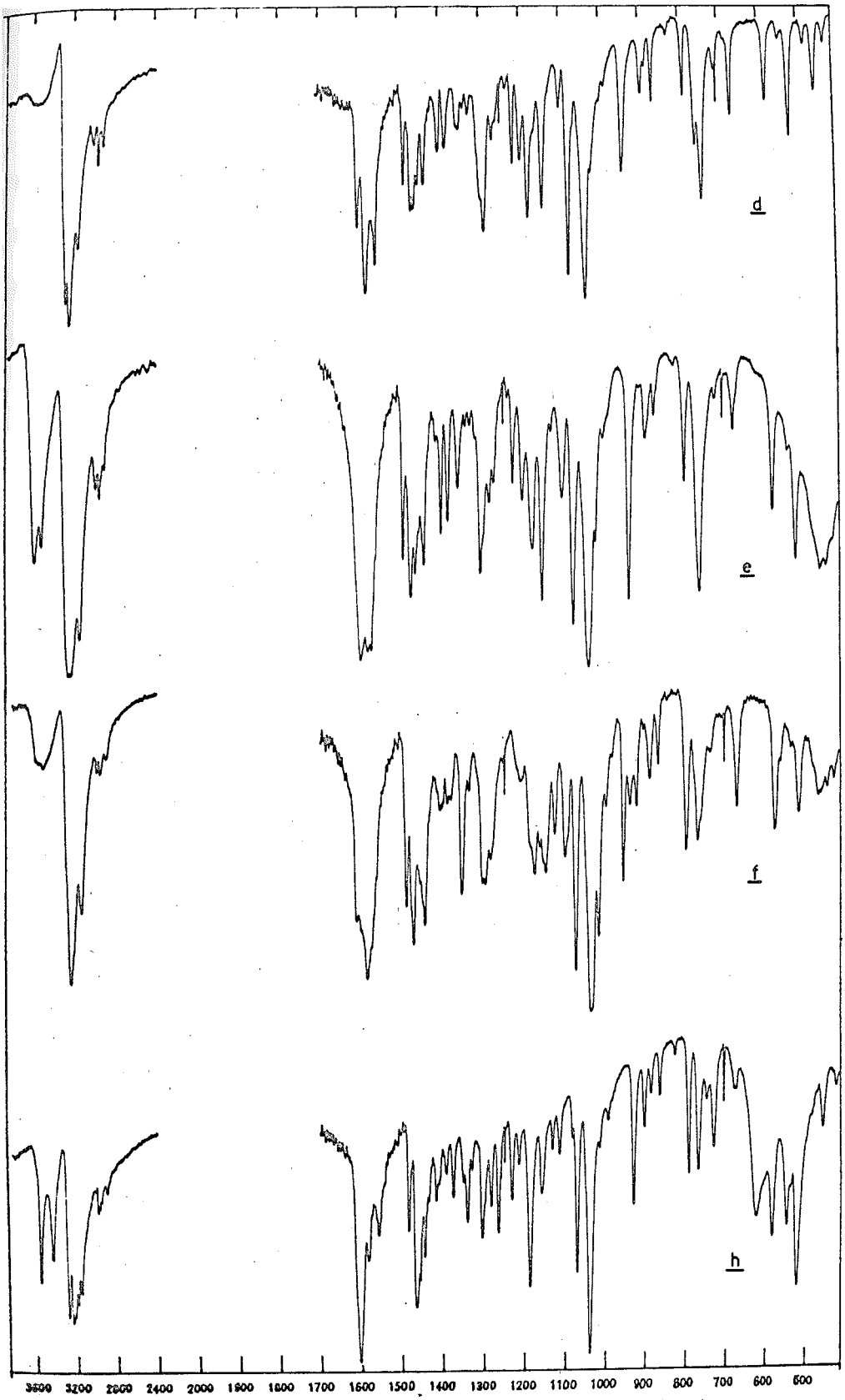


Figure 2.10 Infrared spectra of d, e, f and h - $[Co(tmd)(dien)Cl]ZnCl_4.xH_2O$ in the region 4000-400 cm^{-1} (KBr Disc).

were left to stand at room temperature overnight and the product was collected, washed with 2-propanol and then ether. The results were:

a → a; b → a; c → a; d → a; e → a; f → a; g → a; h → a.

(c) Base Hydrolysis (80°): The above base hydrolysis reactions were repeated, except that the alkaine solutions were heated at 80° for 20 min. Identical isomeric interconversions were obtained.

(d) Reaction with Nitrous Acid: The pure $[Co(tmd)(dien)Cl]ZnCl_4$ isomers were treated with NO_2^-/HCl and $[Co(tmd)(dien)NO_2]ZnCl_4$ salts were obtained (see later). The results were a → b, b → b, c → c, d → d, e → d, f → d, "g" → d, h → h. The pure a, b, c, d and h-$[Co(tmd)(dien)NO_2]ZnCl_4$ salts were decomposed, by heating (80°) a solution of each in 3 F HCl for 1 hour. The $ZnCl_4^{2-}$ salts of the chloro complexes deposited on the addition of $ZnCl_2$. The transformations that resulted were: a → b; b → b; c → c; f → d; h → h.

a and d-Chloro(1,3-propanediamine)(diethylenetriamine) cobalt(III) Tetrachlorocadmiumate(II): The a and d isomers of $[Co(tmd)(dien)Cl]ZnCl_4$ (0.20 g) were separately dissolved in 60° 0.2 F CH_3CO_2H (20 ml) and 12 F HCl (10 ml) containing $CdCl_2$ (2.5 g) was added. The red and purple-red products that slowly deposited on cooling to room temperature were

collected from ice cooled solutions and were washed with 2-propanol and then ether. The yields were a 55.6%, d 87.9%.

b-Chloro(1,3-propanediamine)(diethylenetriamine)cobalt(III) Tetrabromozincate(II): The b isomer of $[Co(tmd)(dien)Cl]ZnCl_4$ (0.25 g) was dissolved in 40° 0.2 F CH_3CO_2H (25 ml) and 63% HBr (15 ml) containing $ZnBr_2$ (2.5 g) was added. The red product (83.8%) that deposited immediately was collected from the ice cooled solution and was washed with 2-propanol and then ether. The yield was 83.8%.

a and d-Chloro(1,3-propanediamine)(diethylenetriamine) cobalt(III) Tetrabromocadmiumate(II): The a and d isomers of $[Co(tmd)(dien)Cl]ZnCl_4$ (0.20 g and 0.25 g respectively) were separately dissolved in 0.2 F CH_3CO_2H at 40° (20 ml, 10 ml) and 63% HBr (5 ml, 5 ml) containing $CdBr_2.4H_2O$ (5 g, 2.5 g) was added. The red and purple-red products deposited immediately. The products were collected from the ice cooled solutions and were washed with 2-propanol and then ether. The yields were: a 77.8%, d 76.8%.

d-Chloro(1,3-propanediamine)(diethylenetriamine)cobalt(III) Tetrachlorocuprate(II): 0.25 g of d-$[Co(tmd)(dien)Cl]ZnCl_4$ was dissolved in 0.2 F CH_3CO_2H (10 ml) at room temperature and 12 F HCl (10 ml) containing $CuCl_2.2H_2O$ (4 g) was added. The orange-red crystals that deposited on cooling in an ice

bath were collected and washed with 2-propanol and then ether. The yield was 21.2%.

a and d-Chloro(1,3-propanediamine)(diethylenetriamine) cobalt(III) Di-iodide: The a and d isomers of $[Co(tmd)(dien)Cl]ZnCl_4$ (0.1 g, 0.1 g respectively) were dissolved in 0.2 F CH_3CO_2H (5 ml, 5 ml) and a solution of NaI (2.5 g, 5.0 g) in water (5 ml, 10 ml) was added. The products that slowly deposited on cooling the solutions in an ice bath were collected, washed with 2-propanol, acetone and then ether. The yields were: a 77.2%, d 55.1%.

a and d-Chloro(1,3-diaminopropane)(diethylenetriamine) cobalt(III) Tetrathiocyanatozincate(II): The a and d isomers of $[Co(tmd)(dien)Cl]ZnCl_4$ were separately dissolved in 80° 0.2 F CH_3CO_2H (0.5 g/60 ml, 0.2 g/30 ml respectively) and a solution of NH_4NCS (1.5 g, 2.5 g) in 5 ml of water was added. The red and purple-red, respectively, tetrathiocyanatozincate(II) salts were deposited slowly on cooling to room temperature. The products were collected from the ice cooled solutions and were washed with 5 ml of ice water. The a isomer was washed with 95% ethanol but the d isomer forms oils with this reagent and it was washed with 2-propanol. The products were air dried. The yields were: a 78%, d 96.0%.

a and e-Chloro(1,3-diaminepropane)(diethylenetriamine) cobalt(III) Perchlorate: The a and e isomers of $[Co(tmd)(dien)Cl]ZnCl_4$ were separately dissolved in 0.2 F $HClO_4$ at 60° (0.25 g/15 ml, 0.5 g/15 ml, respectively) and $NaClO_4.H_2O$ (5 g, 5 g) was added. The red perchlorate salts that crystallised on cooling in an ice bath, were collected, washed with 2-propanol and then ether. The yields were: a 60%, e 20.5%.

a and d-Bromo(1,3-propanediamine)(diethylenetriamine) cobalt(III) Tetrabromozincate(II): $[Co_2(tmd)_2(dien)_2O_2](ClO_4)_4.2H_2O$ (4 g) was added to a solution of 10 ml 63% HBr in 20 ml of water. The solution was heated on a steam bath (ca. 80°) for 1 hour during which time there was mild effervescence and some bromine was evolved. $ZnBr_2$ (4 g) was then added and the product that deposited was collected, washed with 2-propanol and then ether. The crude product was recrystallised by dissolving it in 0.1 F HBr at 60° (total yield in 35 ml) and adding 63% HBr (5 ml) and $ZnBr_2$ (5 g). The product that deposited on cooling was collected in fractions and it was washed and dried as above. The yield was 66.5%. The isomeric composition of the fractions is listed in Table 2.22.

Table 2.22

Isomeric Composition of the $[Co(tmd)(dien)Br]ZnBr_4$ Fractions

Crop	Yield(g)	Isomer(s)	Crop	Yield(g)	Isomer(s)
1	0.19	d	8	0.08	d
2	1.05	d	9	0.15	d
3	1.35	d	10	0.11	d*+a
4	0.11	d*+a	11	0.24	d
5	0.35	d	12	0.14	d
6	0.03	d*+a	13	0.24	d
7	0.04	d*+a			

* Indicates the major component in the fraction

d-Bromo(1,3-diaminopropane)(diethylenetriamine)cobalt(III) Tetrabromocadmiumate(II):

Method A: d-[Co(tmd)(dien)Br]$ZnBr_4$ (0.25 g) was dissolved in 0.2 F CH_3CO_2H (15 ml) at 60° and 63% HBr (5 ml) containing $CdBr_2.4H_2O$ (1.5 g) was added. On cooling to room temperature, the purple product was deposited and this was collected from the ice cooled solution and washed with 2-propanol and then ether. The yield was 85.5%.

Method B: a-[Co(tmd)(dien)Cl]$ZnCl_4$ (0.25 g) was dissolved in water (60 ml) and 50% HBr (10 ml) was added. The solution was boiled under reflux for 20 min. A solution of 40% HBr (15 ml) containing $CdBr_2.4H_2O$ (4 g) was then added and on cooling to room temperature the product was deposited. It was collected in two crops and was washed with 2-propanol and then ether. The second crop contained the a isomer as a minor component. The yield was 85.6%.

h-Bromo(1,3-propanediamine)(diethylenetriamine)cobalt(III) Tetrabromocadmiumate(II): h-[Co(tmd)(dien)Cl]$ZnCl_4.H_2O$ (0.1 g) was dissolved in water (12 ml) and 50% HBr (10 ml) was added. The solution was boiled under reflux for 40 min. A solution of 50% HBr (10 ml) containing $CdBr_2.4H_2O$ (4 g) was then added. On cooling in an ice bath, the product was slowly deposited and it was collected, washed with 2-propanol and then ether. The yield was 55.8%.

d-Bromo(1,3-propanediamine)(diethylenetriamine)cobalt(III) Tetrachlorozincate(II): d-$[Co(tmd)(dien)Br]ZnBr_4$ (0.2 g) was dissolved in 0.2 F CH_3CO_2H (10 ml) at 40°, and a solution of 12 F HCl (5 ml) containing $ZnCl_2$ (2.5 g) was added. After cooling the solution in an ice bath for 24 hours, the purple crystalline product that was slowly deposited was collected, washed with 2-propanol and then ether. The yield was quantitative.

d-Bromo(1,3-propanediamine)(diethylenetriamine)cobalt(III) Tetrathiocyanatozincate(II): d-$[Co(tmd)(dien)Br]ZnBr_4$ (0.2 g) was dissolved in 0.2 F CH_3CO_2H (40 ml) at 60° and a solution of NH_4SCN (2.5 g) and $Zn(ClO_4)_2$ (2 g) in water (5 ml) was added. On standing at room temperature overnight, the purple-red crystalline product was deposited and it was collected, washed with 2-propanol and air dried. The yield was 83.7%.

d-Azido(1,3-propanediamine)(diethylenetriamine)cobalt(III) Tetrabromocadmiumate(II): e-$[Co(tmd)(dien)Cl]ZnCl_4.H_2O$ (0.65 g) was dissolved in 0.2 F CH_3CO_2H (25 ml) and NaN_3 (2.5 g) was added. The solution was boiled under reflux for 30 min. A solution of 50% HBr (20 ml) containing $CdBr_2.4H_2O$ (5 g) was then added. After cooling in an ice bath for 30 min. the red-purple product slowly crystallised and it was collected in crops, washed with 2-propanol and then ether.

The crude product was recrystallised by dissolving it in 0.2 F CH_3CO_2H at 40° (0.1 g/10 ml) and then adding 50% HBr (10 ml/0.1 g) and $CdBr_2.4H_2O$ (1 g/0.1 g). The product that deposited on cooling was collected from the ice cooled solution and was washed and dried as above. The yield was 23.1%.

b, c, f-Nitro(1,3-propanediamine)(diethylenetriamine) cobalt(III) Tetrachlorozincate(II): The a, b, c, d, e, f and "g" isomers of $[Co(tmd)(dien)Cl]ZnCl_4$ were separately dissolved in 0.2 F HCl (0.5 g/12.5 ml, 0.15 g/10 ml, 0.10 g/ 5 ml, 0.25 g/10 ml, 0.25 g/10 ml, 0.25 g/10 ml and 1 g/25 ml respectively) and $NaNO_2$ (2 g, 1 g, 0.5 g, 1 g, 1 g, 1 g, 3 g) was added. The solutions were heated on a steam bath (ca. 80°) for 30 min. during which time mild effervescence occurred and the colour changed from red to orange-yellow. The hot solutions were poured slowly into 1:1 2-propanol/ acetone (50 ml, 20 ml, 12.5 ml, 25 ml, 25 ml, 25 ml, 100 ml) containing $ZnCl_2$ (2,5 g, 1 g, 0.5 g, 1 g, 1 g, 1 g, 2.5 g) and 12 F HCl (1 ml, 0.2 ml, 0.2 ml, 0.5 ml, 0.5 ml, 0.5 ml, 0.5 ml). The yellow crystals that deposited on cooling to room temperature were collected, washed with acetone and then ether. The yields were a → b 68.4%, b → b 65.4%, c → c 74.0%, d → f 70.1%, e → f 60.1%, f → f 70.3% and "g" → f 84.2%.

h-Nitro(1,3-propanediamine)(diethylenetriamine)cobalt(III) Tetrachlorozincate(II): h-[Co(tmd)(dien)Cl]$ZnCl_4$.H_2O (0.2 g) was dissolved in 0.2 F CH_3CO_2H (15 ml) and $NaNO_2$ (1 g) was added. The solution was boiled under reflux for 30 min. during which time the colour changed from purple-red to orange-yellow. The hot solution was slowly poured into 1:1 2-propanol/acetone (25 ml) containing $ZnCl_2$ (1 g) and 12 F HCl (0.5 ml). After standing the solution at 0-5° for 3 days, the yellow-orange product that slowly deposited was collected, washed with 2-propanol, acetone and ether. The yield was 45.3%.

f-Nitro(1,3-propanediamine)(diethylenetriamine)cobalt(III) Tetrabromocadmiumate(II): d-[Co(tmd)(dien)Br]$ZnBr_4$ (0.3 g) was dissolved in 0.2 F HBr (8 ml) and $NaNO_2$ (1.5 g) was added. The solution was heated on a steam bath (ca. 80°) for 30 min. during which time a mild effervescence occurred and the colour changed from red-purple to orange-yellow. The hot solution was slowly poured into 1:1 2-propanol/acetone (30 ml) containing $CdBr_2.4H_2O$ (2 g) and 63% HBr (1 ml). On cooling to room temperature, the yellow product that slowly deposited was collected, washed with acetone and ether. The yield was 53.6%.

Table 2.23

Analytical Data for [Co(tmd)(dien)X]Y

Complex	Calculated					Found				
	C%	H%	N%	Co%	X%*	C%	H%	N%	Co%	X%*
$[Co_2(tmd)_2(dien)_2O_2](ClO_4)_4 \cdot 2H_2O$	17.92	5.37	14.93	12.56		18.33	5.21	15.07	12.65	
$[Co(tmd)(dien)Cl]ZnCl_4$ - a	17.56	4.84		12.30	37.02	17.73	4.78		12.25	37.07
- b						17.63	4.78		12.41	37.22
- c						17.32	4.69		12.82	36.91
- d						17.49	4.73		12.36	36.91
- f						17.64	4.75		12.45	36.83
- g**						17.51	4.83		12.25	36.35
$[Co(tmd)(dien)Cl]ZnCl_4 \cdot H_2O$ - e	16.92	5.07		11.86	35.68	17.04	4.95		11.92	35.87
- h						16.95	4.98		11.89	35.60
$[Co(tmd)(dien)Cl]CdCl_4$ - a				11.21	33.71				11.25	33.61
- d									11.10	33.75
$[Co(tmd)(dien)Cl]ZnBr_4$ - b				8.98	54.07				8.85	53.98
- d				8.98	54.07				8.90	54.00

Table 2.23 (contd.)

Complex	Calculated					Found				
	C%	H%	N%	Co%	X%*	C%	H%	N%	Co%	X%*
$[Co(tmd)(dien)Cl]CdBr_4$ - a	11.95	3.29		8.38	50.46	12.46	3.54		8.35	50.57
- d						12.12	3.32		8.42	50.40
$[Co(tmd)(dien)Cl]CuCl_4$ - d	17.62	4.86		12.35	37.16	17.46	4.79		12.41	36.82
$[Co(tmd)(dien)Cl]I_2$ - a				11.22	55.05				11.20	55.00
- d									11.09	54.90
- h									11.15	55.08
$[Co(tmd)(dien)Cl]Zn(SCN)_4$ - a				10.35	47.04				10.27	47.35
- d									10.21	47.23
$[Co(tmd)(dien)Cl](ClO_4)_2$ - a	17.86	4.92		12.52	7.53	17.85	5.06		12.42	7.62
- e						17.99	5.02		12.35	7.75
$[Co(tmd)(dien)Br]ZnBr_4$ - a	11.99	3.31		8.41	56.99	12.35	3.50		8.28	56.51
						12.42	3.41		8.35	57.15
$[Co(tmd)(dien)Br]CdBr_4$ - d	11.24	3.10		7.88	53.41				7.85	53.35
- h						11.50	3.17		7.81	53.49

Table 2.23 (contd.)

Complex	Calculated					Found				
	C%	H%	N%	Co%	X%*	C%	H%	N%	Co%	X%*
$[Co(tmd)(dien)Br]ZnCl_4$ - d				11.26	42.37				11.25	42.15
$[Co(tmd)(dien)Br]Zn(SCN)_4$ - d				9.61	50.86				9.52	50.50
$[Co(tmd)(dien)N_3]CdBr_4$ - d	11.84	3.26		8.30	45.00	12.10	3.41		8.25	44.65
$[Co(tmd)(dien)NO_2]ZnCl_4$ - b	17.18	4.774		12.04	28.97	17.54	4.78		12.05	28.91
- c						17.49	4.82		12.12	28.80
- f						17.48	4.75		11.96	28.75
- h						17.17	4.97		12.05	28.86
$[Co(tmd)(dien)NO_2]CdBr_4$ - f				8.25	44.75				8.32	44.62
$[Co(tmd)(dien)NO_2]Zn(SCN)_4$ - f	22.97	4.00		10.17	40.05				10.12	40.25

* Total halogen or NCS^- as found by Ag^+ titration

** Shown to be an approximately 3:1 mixture of f-$[Co(tmd)(dien)Cl]ZnCl_4$ and d-$[Co(tmd)(dien)NO_2]ZnCl_4$

f-Nitro(1,3-propanediamine)(diethylenetriamine)cobalt(III) Tetrathiocyanatozincate(II): f-$[Co(tmd)(dien)NO_2]ZnCl_4$ (0.2 g) was dissolved in 0.2 F CH_3CO_2H (35 ml) at 80° and NH_4SCN (1.5 g) dissolved in water (5 ml) was added. On cooling to room temperature, the yellow product that slowly deposited was collected, washed with 2-propanol and air dried. The yield was 75.0%.

(2) N-methyl-1,3-propanediamine

Analytical data for the complexes are presented in Table 2.26. Infrared spectra of the chloro $ZnCl_4^{2-}$ salts in the region 4000-400 cm^{-1} are presented in Fig. 2.11 and 2.12.

Isomers of Chloro(N-methyl-1,3-propanediamine)(diethylene-triamine) cobalt(III) Tetrachlorozincate(II):

Method A: Trans-$Co(dien)Cl_3$ (8 g) was suspended in water (25 ml) and N-methyl-1,3-propanediamine(2.5 ml, 100%) was added. The mixture was warmed at ca. 60° for 30 min. during which time the brown solid dissolved giving a red-purple solution. The solution was cooled in an ice bath and then 12 F HCl (25 ml) containing $ZnCl_2$ (12 g) was added. On standing the resultant red-brown solution at room temperature the crude complex was slowly deposited and it was collected in crops, washed with 2-propanol and then ether. The crude complex was recrystallised by dissolving it in 0.2 F CH_3CO_2H at 60° (2 g/60 ml) and then adding 12 F HCl (10 ml/

1 g) containing $ZnCl_2$ (2.5 g/1 g). The purified complex that was deposited on cooling the solution to room temperature was collected in fractions and was washed and dried as above.

The aqueous mother liquor deposited further crops of crude complex on slow evaporation at room temperature and these were recrystallised as above but using a corresponding reduction in the weights and volumes of the reagents used.

The total yield of chloropentaamine complex was 9.44 g or 64.2%. The isomeric composition of each fraction of recrystallised product is listed in Table 2.24.

Method B: trans-$Co(dien)(NO_2)_3$ (14 g) was suspended in water (30 ml) and N-methyl-1,3-propanediamine (4.5 ml, 100%) and activated charcoal (2 g) were added. The solution was heated on a steam bath (ca. 80°) for 30 min. during which time much of the insoluble neutral complex dissolved. The solution was filtered and the residue, that contained 6 g of Cobalt complex starting material, was washed with distilled water (60 ml). The combined filtrates were cooled in an ice bath and 12 F HCl (25 ml) was slowly added. The solution was reheated on a steam bath (ca. 80°) and $ZnCl_2$ (15 g) was added. After 30 min., the purple product commenced to crystallise and it was collected in crops, washed with 2-propanol and then ether.

Table 2.24

Isomeric Compositions of fractions of $[Co(Me\text{-}tmd)(dien)Cl]ZnCl_4$; Method A

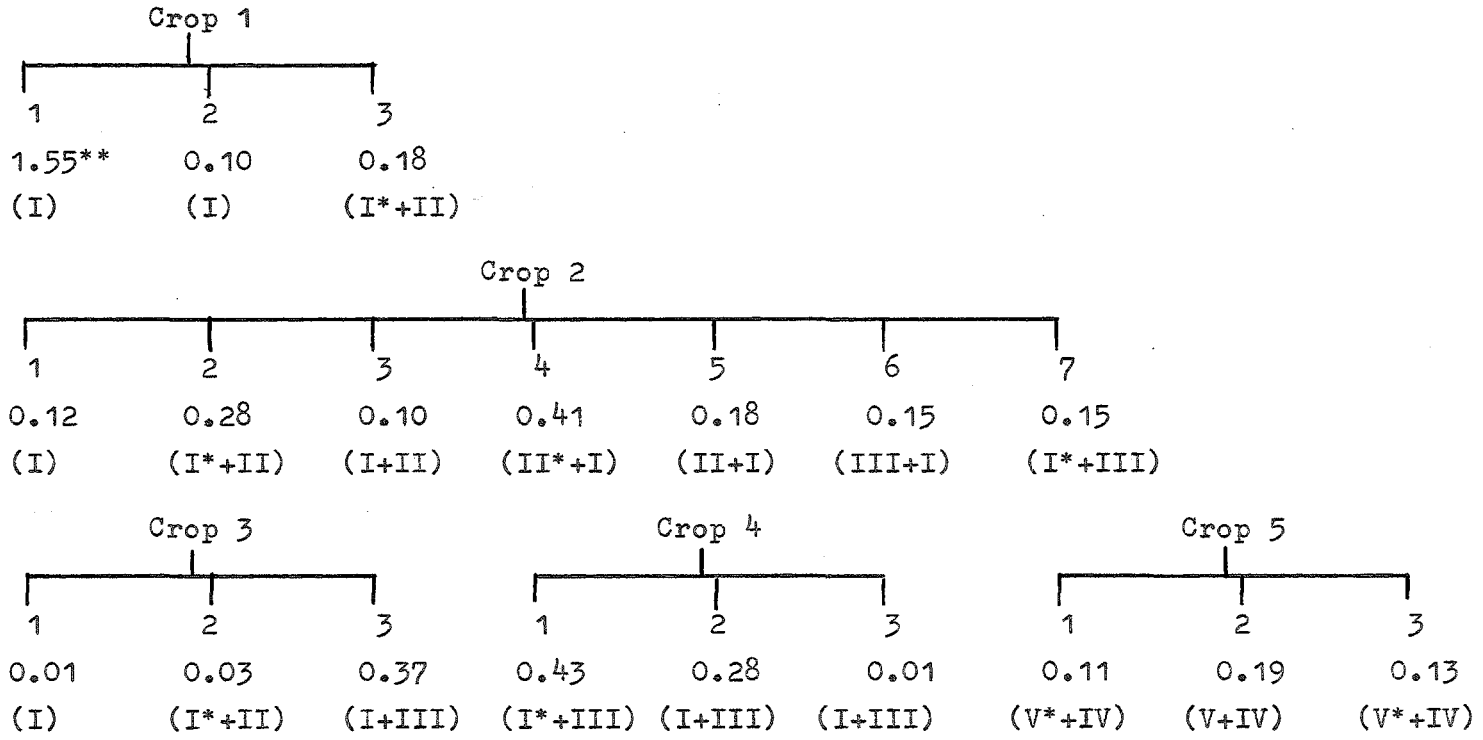
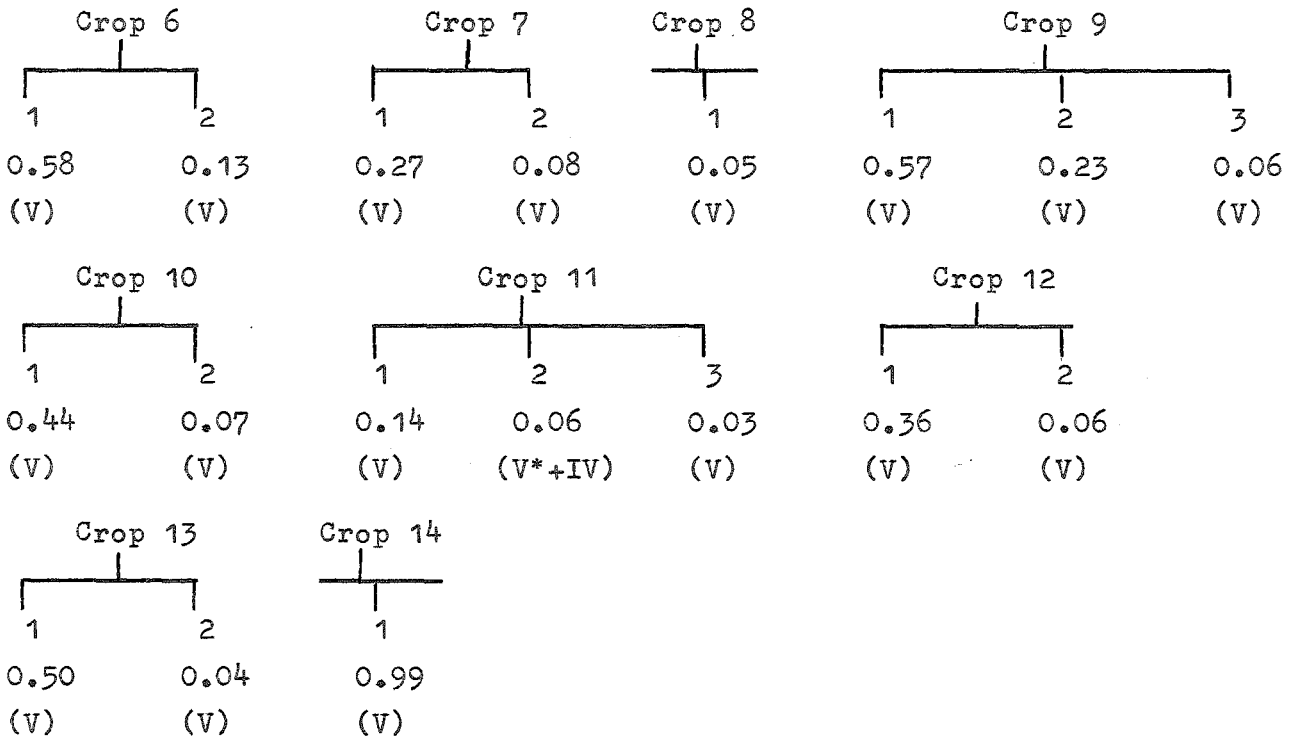


Table 2.24 (contd.)



* denotes major component of fraction

** weight in g

The crude product was recrystallised by dissolving it in 0.2 F CH_2CO_2H (1 g/50 ml) containing $ZnCl_2$ (2.5 g/1 g). The purified product that deposited on cooling the solution to room temperature, was collected in fractions, washed and dried as above.

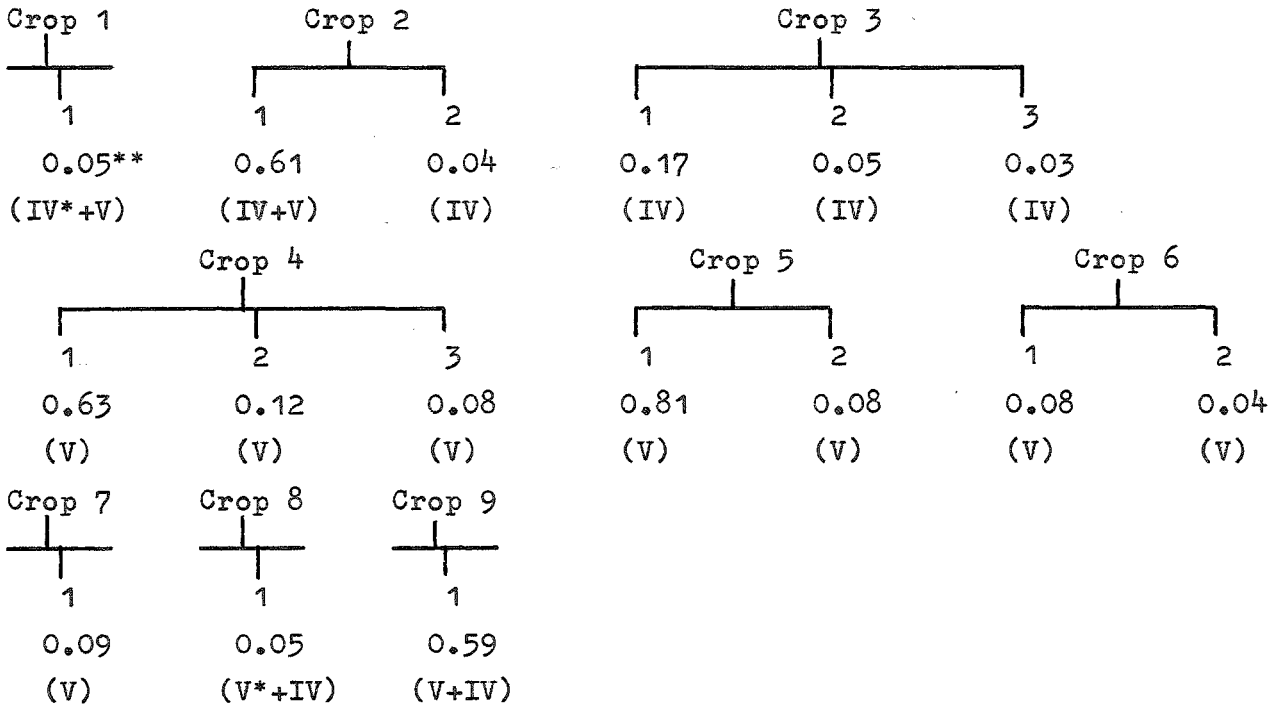
On slow evaporation of the aqueous mother liquor at room temperature, further crops of crude product were obtained and these were recrystallised as above but using a corresponding reduction in the weights and volumes of the reagents used.

The total yield of chloropentaamine complex was 3.52 g or 26.8%. The isomeric composition of each fraction of recrystallised product is listed in Table 2.25.

I and V-Chloro(N-methyl-1,3-propanediamine)(diethylene-triamine) cobalt(III)Tetrabromozincate(II): The I and V isomers of $[Co(Me\text{-}tmd)(dien)Cl]ZnCl_4$ were separately dissolved in 0.2 F CH_3CO_2H at 40° (0.25 g/10 ml, 0.25 g/25 ml, respectively) and a solution of 63% HBr (10 ml, 10 ml) containing $ZnBr_2$ (2.5 g, 3.0 g) was added. The red-brown and purple products were deposited immediately and they were collected from the ice cooled solutions, washed with 2-propanol and then ether. The yields were I 72.3% and V 89.4%.

Table 2.25

Isomeric Compositions of Fractions of $[Co(Me\text{-}tmd)(dien)Cl]ZnCl_4$; Method B



* denotes major component of fraction

** weight in g

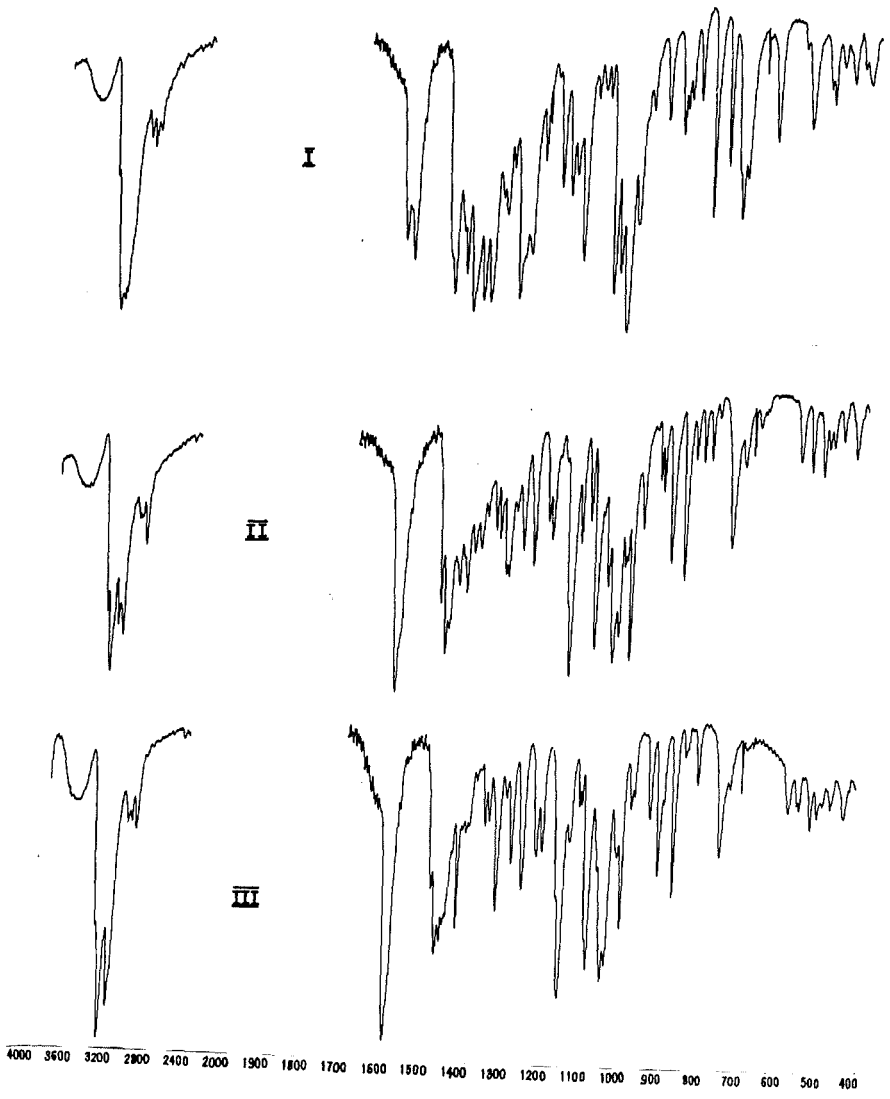


Figure 2.11 Infrared spectra of I, II and III - $[Co(Me\text{-}tmd)(dien)Cl]ZnCl_4$ in the region 4000-400 cm^{-1} (KBr Disc).

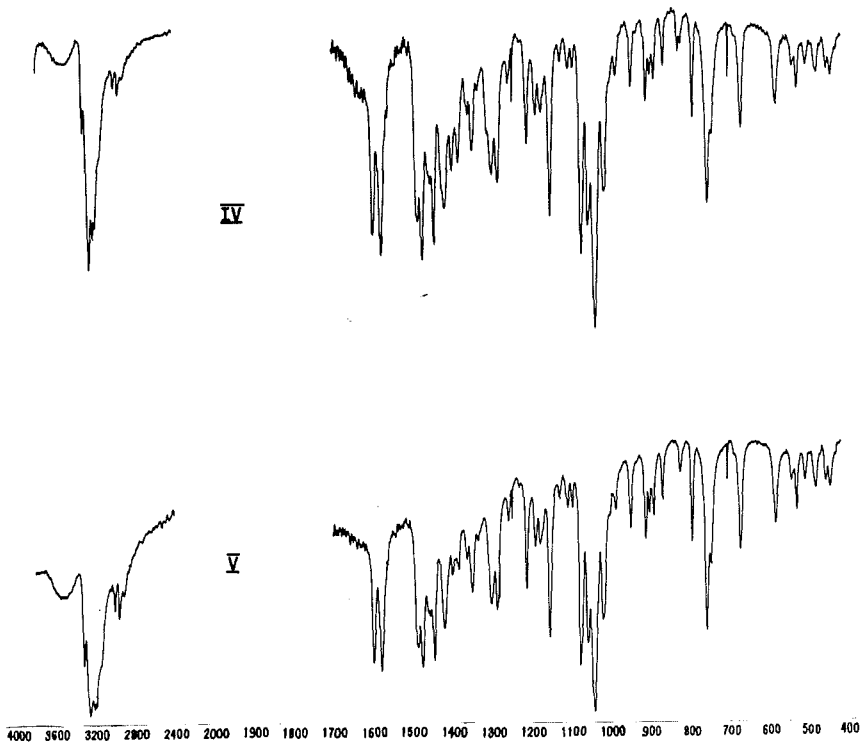


Figure 2.12 Infrared spectra of IV and V - $[Co(Me\text{-}tmd)(dien)Cl]ZnCl_4$ in the region 4000-400 cm^{-1} (KBr Disc).

III and V-Bromo(N-methyl-1,3-propanediamine)(diethylene-triamine) cobalt(III) Tetrabromocadmiumate(II): V-[Co(Me-tmd)(dien)Cl]$ZnCl_4$ (0.90 g) was dissolved in water (15 ml) and 50% HBr (10 ml) was added. The solution was boiled under reflux for 45 min. The hot solution was slowly poured into a solution of 50% HBr (15 ml) containing $CdBr_2.4H_2O$ (4 g) and the product that deposited on cooling to room temperature was collected in crops, washed with 2-propanol and then ether. The isomeric composition of the crops was:

Crop No.	Weight(g)	Composition
1	0.35	V
2	0.13	V
3	0.33	V* + III
4	0.25	V + III

*denotes major component of crop

The total yield of bromopentaamine complex was 1.06 g or 75.4%.

A similar synthesis using I-[Co(Me-tmd)(dien)Cl]$ZnCl_4$ as the starting material resulted in the formation of a mixture of the III and V isomers in a 73.5% yield.

V-Bromo(N-methyl-1,3-propanediamine)(diethylenetriamine) cobalt(III) Tetrachlorozincate(II): V-[Co(Me-tmd)(dien)Br] $CdBr_4$ (0.15 g) was dissolved in 0.2 F CH_3CO_2H (35 ml) at 45° and a solution of 12 F HCl (10 ml) containing $ZnCl_2$ (2.5 g) was added. On cooling the solution to room temperature the purple product that was deposited was collected, washed with 2-propanol and then ether. The yield was 68.0%.

V-Azido(N-methyl-1,3-propanediamine)(diethylenetriamine) cobalt(III) Tetrabromocadmiumate(II): V-[Co(Me-tmd)(dien) Cl]$ZnCl_4$ (0.25 g) was dissolved in 0.2 F CH_3CO_2H (10 ml) and NaN_3 (1.5 g) was added. The solution was heated on a steam bath (ca. 80°) for 30 min. and then a solution of 50% HBr (10 ml) containing $CdBr_2.4H_2O$ (2.5 g) was added. On cooling the solution in an ice bath, the purple-red product, that was slowly deposited, was collected in crops, washed with 2-propanol and then ether. The yield was 62.2%. The final crop contained an appreciable amount of the III isomer.

I-Nitro(N-methyl-1,3-propanediamine)(diethylenetriamine) cobalt(III) Tetrachlorozincate(II): V-[Co(Me-tmd)(dien)Cl] $ZnCl_4$ (0.5 g) was dissolved in 0.2 F HCl (12.5 ml) and $NaNO_2$ (2 g) was added. The solution was heated on a steam bath (ca. 80°) for 30 min. during which time the mild

effervescence subsided and the colour changed from purple-red to orange. The hot solution was slowly poured into 1:1 2-propanol/acetone (50 ml) containing 12 F HCl (1 ml) and $ZnCl_2$ (2.5 g). On cooling the solution to room temperature the yellow product deposited and it was collected from the ice cooled solution, washed with acetone and then ether. The yield was 69.0%. The same product was formed when I-$[Co(Me\text{-}tmd)(dien)Cl]ZnCl_4$ was used as the starting material.

Resolution of V-$Co(Me\text{-}tmd)(dien)Cl^{2+}$

V-$[Co(Me\text{-}tmd)(dien)Cl]ZnCl_4$ (0.5 g) together with ammonium (+)-α-Bromo-Camphor-π-Sulphonate were dissolved in 0.1 F HCl (15 ml) at 50° and the solution was allowed to stand at room temperature. After two hours, the violet crystals that were slowly deposited were collected, washed with 2-propanol and then ether. The (+)BCS complex was converted to the tetrachlorozincate(II) salt by dissolving it in 6 F HCl (0.1 g/25 ml) at 40°, and then adding $ZnCl_2$ (5 g/0.1 g). The product that was deposited immediately was collected, washed and dried as above. Three further successive crops of the (+)BCS salt deposited over a period of 24 hours were treated in the same manner as above.

12 F HCl (25 ml) containing $ZnCl_2$ (2.5 g) was then added to the aqueous mother liquor and the product that deposited immediately was collected, washed and dried as

above.

All crops were recrystallised to constant rotation.

Crop No.	Weight(g)	$[M]_{534}$*	Optical Purity
1	0.016	-3165°	94.5%
2	0.134	-3363°	100%
3	0.017	-3363°	100%
4	0.013	-3217°	96.5%
5	0.217	+3251°	96.7%
6	0.039	+3312°	98.6%

*Units are deg.dm^{-1}(M/100 cm^3)$^{-1}$

A solution of $(+)_{589}$-V-Co(Me-tmd)(dien)Cl^{2+} (assumed optically pure) in 0.1 F $HClO_4$ has $[M]_{618}$ = +533.1 , $[M]_{594}$ = 0 , $[M]_{534}$ = -3363 , $[M]_{472}$ = 0 , $[M]_{448}$ = +661.3 , $[M]_{410}$ = +101.0 , $[M]_{386}$ = 375.3 , $[M]_{373}$ = 0 .
A solution of 98.6% optically pure (based on the (+) isomer) $(-)_{589}$-V-Co(Me-tmd)(dien)Cl^{2+} in 0.1 F $HClO_4$ has $[M]_{618}$ = -527.5 , $[M]_{594}$ = 0 , $[M]_{534}$ = +3310 , $[M]_{472}$ = 0 , $[M]_{448}$ = -651.5 , $[M]_{410}$ = -99.4 , $[M]_{386}$ = -369.0 , $[M]_{373}$ = 0 .

Resolution of I-Co(Me-tmd)(dien)Cl^{2+}

I-[Co(Me-tmd)(dien)Cl]$ZnCl_4$ (1 g) and Ammonium (+)-α-bromo-Camphor-π-Sulphonate (1 g) were dissolved in 0.1 F HCl (20 ml) at 50° and the solution was allowed to

stand at room temperature. After four days the brown product that was deposited slowly was separated from the mother liquor by decantation and it was then dissolved in 6 F HCl (15 ml) at 70°. On the addition of $ZnCl_2$ (2.5 g) the tetrachlorozincate(II) salt was deposited and this was collected from the ice cooled solution, washed with 2-propanol and then ether. Two further successive crops that deposited over a period of five days were treated in the same manner as above.

12 F HCl (25 ml) containing $ZnCl_2$ (4 g) was then added to the aqueous mother liquor and the product that deposited immediately was collected, washed and dried as above.

All crops were recrystallised to constant rotation.

Crop No.	Weight(g)	$[M]_{530}$*
1	0.100	-246.1°
2	0.089	-242.2°
3	0.112	-234.2°
4	0.522	+11.8°

*Units are $deg.dm^{-1}(M/100\ cm^3)^{-1}$

A solution of the fraction having the maximum rotation of (+)589-I-Co(Me-tmd)(dien)Cl^{2+} in 0.1 F $HClO_4$ has $[M]_{615}$ = +41.0°, $[M]_{593}$ = 0°, $[M]_{530}$ = -246.1°, $[M]_{452}$ = 0°,

$[M]_{432}$ = +23.4°, $[M]_{410}$ = +15.6°, $[M]_{384}$ = +61.7°, $[M]_{368}$ = = 0°.

A solution of $(-)_{589}$ -I- $Co(Me\text{-}tmd)(dien)Cl^{2+}$ in 0.1 F $HClO_4$ has $[M]_{615}$ = - 16.6°, $[M]_{593}$ = 0°, $[M]_{530}$ = +111.5°, $[M]_{452}$ = 0°, $[M]_{432}$ = -13.1°, $[M]_{410}$ = -7.8°, $[M]_{384}$ = 27.7°, $[M]_{368}$ = 0°

Qualitative Isomerisation Reactions

(a) Base Hydrolysis: The I, II, III, IV and V isomers of $[Co(Me\text{-}tmd)(dien)Cl]ZnCl_4$ were separately dissolved in water (0.05 g/5 ml) and NaOH (0.5 g) was then added. The solution was heated (ca. 70°) for 5 min. and then 12 F HCl (5 ml) containing $ZnCl_2$ (1 g) was added. The solutions were allowed to cool to room temperature and the product that deposited overnight was collected, washed with 2-propanol and then ether. The transformations that resulted were I → V; II → IV; III → V; IV → IV; V → V.

(b) Reaction with Nitrous Acid: The nitro complexes derived from the I and V isomers of $[Co(Me\text{-}tmd)(dien)Cl]ZnCl_4$ were prepared by the method described before. These were decomposed by heating (ca. 80°) a solution of each in 3 F HCl for 2 hours. The $ZnCl_4^{2-}$ salts of the chloro isomers generated in this manner were deposited by the addition of $ZnCl_2$. The transformations that resulted were I → I; V → I.

Table 2.26

Analytical Data for [Co(Me-tmd)(dien)X]Y

Complex	Calculated				Found			
	C%	H%	Co%	X%[a]	C%	H%	Co%	X%[a]
$[Co(Me\text{-}tmd)(dien)Cl]ZnCl_4$ - I	19.50	5.11	11.96	35.96	19.40	5.06	11.90	35.83
- II					19.57	5.03	11.92	35.99
- III					19.79	5.14	11.98	35.90
- IV					19.59	5.05	11.90	35.92
- V					19.71	5.06	11.88	35.93
$[Co(Me\text{-}tmd)(dien)Cl]ZnBr_4$ - I			8.79	52.95			8.72	52.85
- V							8.69	52.82
$[Co(Me\text{-}tmd)(dien)Br]CdBr_4$ - III			7.73	52.42			7.65	52.57
- V							7.70	52.48
$[Co(Me\text{-}tmd)(dien)Br]ZnCl_4$ - V			11.00	41.40			11.05	41.32
$[Co(Me\text{-}tmd)(dien)N_3]CdBr_4$ - V			8.14	44.13			8.22	44.03
$[Co(Me\text{-}tmd)(dien)NO_2]ZnCl_4$ - I			11.75	28.27			11.68	28.15

[a] Total halide as found by Ag^+ titration

(3) N-(n-butyl)-1,3-propanediamine

Analytical data for the complexes are presented in Table 2.28. Infrared spectra of the chloro $ZnCl_4^{2-}$ salts in the region 4000-400 cm^{-1} are presented in Fig. 2.13.

Isomers of Chloro(N-(n-butyl)-1,3-propanediamine)(diethylene-triamine) cobalt(III) Tetrachlorozincate(II): trans - $Co(dien)Cl_3$ (5 g) was suspended in methanol (100 ml) containing NaOH (2 g) and N-(n-butyl)-1,3-propanediamine (3.5 ml) was added. The solution was boiled under reflux for 40 min. and then 12 F HCl (40 ml) containing $ZnCl_2$ (10 g) was slowly added. The solution was cooled in an ice bath and the amine dihydrochloride salt that deposited was separated by filtration. After standing at room temperature for 24 hours the product commenced to deposit and it was collected, washed with 2-propanol and then ether.

The crude product was recrystallised by dissolving it in 0.2 F CH_3CO_2H (0.1 g/10 ml) and then adding 12 F HCl (5 ml/0.1 g) containing $ZnCl_2$ (1 g/0.1 g). The purified product that deposited on cooling was collected in fractions and was washed and dried as above.

The aqueous mother liquor deposited further crops of crude complex and these were recrystallised as above but using a corresponding reduction in the weights and volumes of the reagents used.

The total yield of chloropentaamine complex was 2.86 g or 29.6%. The isomeric composition of each fraction of recrystallised product is listed in Table 2.27.

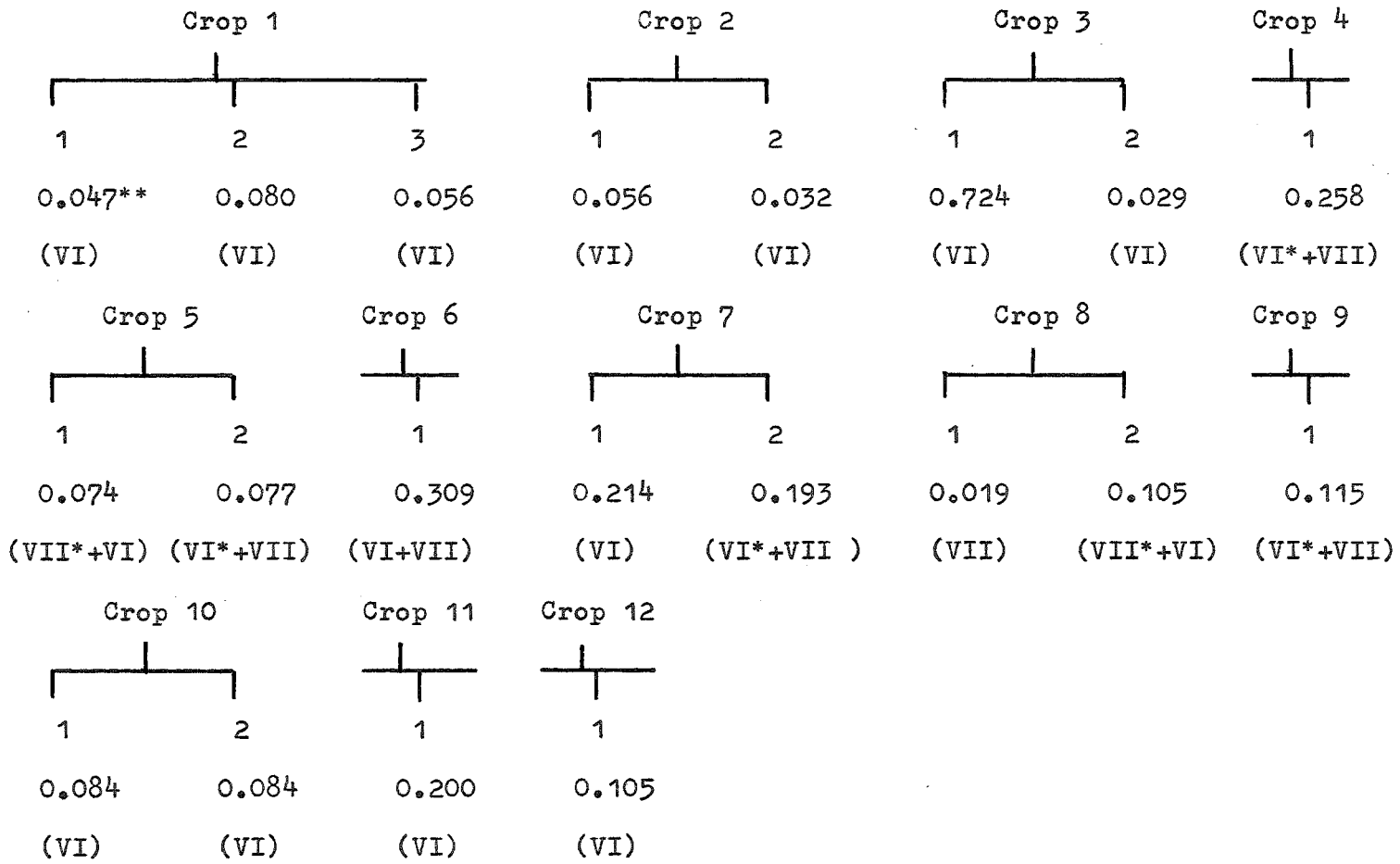
VI-Chloro(N-(n-butyl)-1,3-propanediamine)(diethylene-triamine) cobalt(III) Tetrabromocadmiumate(II): VI-[Co(Bu-tmd)(dien)Cl]$ZnCl_4$ (0.25 g) was dissolved in 0.2 F CH_3CO_2H (15 ml) at 40° and a solution of 30% HBr (20 ml) containing $CdBr_2.4H_2O$ (2.5 g) was added. On cooling the solution to room temperature, the red crystalline product that deposited was collected, washed with 2-propanol and then ether. The yield was 82.1%.

VI-Chloro(N-(n-butyl)-1,3-propanediamine)(diethylene-triamine) cobalt(III) Perchlorate: VI-[Co(Bu-tmd)(dien)Cl]$ZnCl_4$ (0.25 g) was dissolved in 0.2 F CH_3CO_2H (12 ml) at ca. 40° and $NaClO_4.H_2O$ (5 g) was added. The red crystalline product that deposited was collected from the ice cooled solution, washed with 2-propanol and then ether. The yield was 72.8%.

VII-Bromo(N-(n-buryl)-1,3-propanediamine)(diethylene-triamine) cobalt(III) Tetrabromocadmiumate(II) VI-[Co(Bu-tmd)(dien)Cl]$ZnCl_4$ (0.3 g) was dissolved in water (10 ml) and 50% HBr (5 ml) was added. The solution was boiled under reflux for 45 min. and then it was added

Table 2.27

Isomeric Composition: Isomers of $[Co(Bu\text{-}tmd)(dien)Cl]ZnCl_4$



* denotes major component of fraction

** weight in g

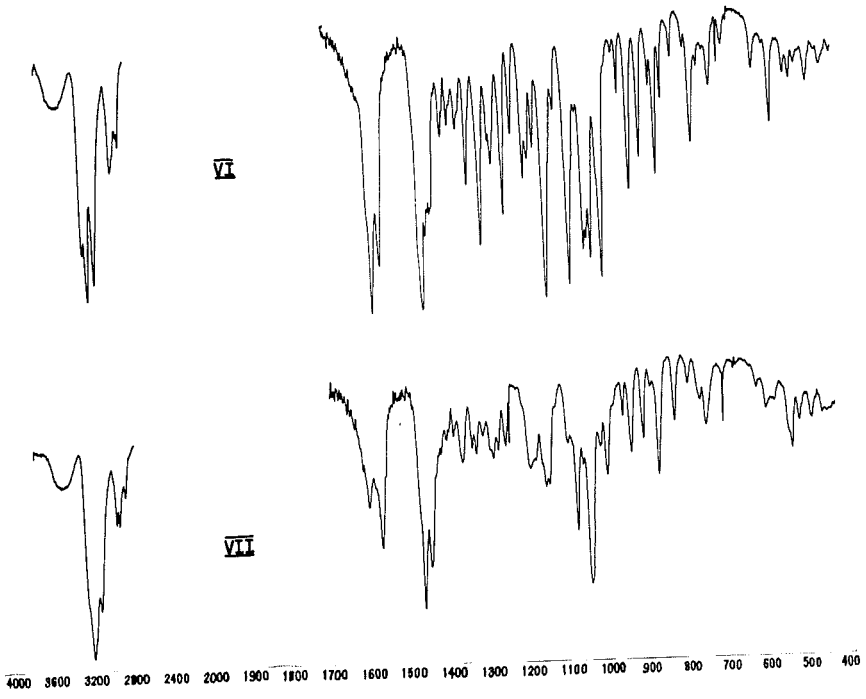


Figure 2.13 Infrared spectra of VI and VII - $[Co(Bu\text{-}tmd)(dien)Cl]ZnCl_4$ in the region 4000-400 cm^{-1} (KBr Disc).

to 50% HBr (10 ml) containing $CdBr_2.4H_2O$ (4 g). On cooling to room temperature the purple product commenced to crystallise and it was collected in crops, washed with 2-propanol and then ether. The yield was 50.7% of the pure VII isomer.

VI-Nitro(N-(n-butyl)-1,3-propanediamine)(diethylenetriamine) cobalt(III) Tetrachlorozincate(II):

VI-$[Co(Bu\text{-}tmd)(dien)Cl]ZnCl_4$ (0.25 g) was dissolved in 0.2 F HCl (10 ml) and $NaNO_2$ (2 g) was added. The solution was heated on a steam bath (ca. 80°) for 15 min. during which time mild effervescence occurred and the colour changed from red to orange. The hot solution was slowly poured into 1:1 acetone/2-propanol (50 ml) containing 12 F HCl (1 ml) and $ZnCl_2$ (2.5 g). On cooling to room temperature, the yellow product that deposited slowly was collected, washed with 2-propanol and then ether. The yield was 42.3%. The product is sparingly soluble in acetone.

(4) N-cyclohexyl-1,3-propanediamine

Analytical data for the complexes are presented in Table 2.30. Infrared spectra of the chloro $ZnCl_4^{2-}$ salts in the region 4000-400 cm^{-1} are presented in Fig. 2.14.

Table 2.28

Analytical Data for [Co(Bu-tmd)(dien)X]Y

Complex	Calculated				Found			
	C%	H%	Co%	X%[a]	C%	H%	Co%	X%[a]
$[Co(Bu\text{-}tmd)(dien)Cl]ZnCl_4$ - VI	24.70	5.84	11.02	33.14	25.31	5.91	11.04	33.07
- VIII					24.65	5.77	11.05	33.01
$[Co(Bu\text{-}tmd)(dien)Cl]CdBr_4$ - VI			7.76	46.74			7.72	45.65
$[Co(Bu\text{-}tmd)(dien)Cl](ClO_4)_2$ - VI			11.19	6.73			11.25	6.65
$[Co(Bu\text{-}tmd)(dien)Br]CdBr_4$ - VII			7.33	49.68			7.25	49.49
$[Co(Bu\text{-}tmd)(dien)NO_2]ZnCl_4$ - VI			10.80	26.00			10.74	26.03

[a] Total halide as found by Ag^+ titration

Isomers of Chloro(N-cyclohexyl-1,3-propanediamine)(diethylenetriamine) cobalt(III) Tetrachlorozincate(II): trans-$Co(dien)Cl_3$ (8 g) was suspended in methanol (180 ml) containing NaOH (2 g) and N-cyclohexyl-1,3-propanediamine (10 ml) was added. The solution was boiled under reflux for 15 min. and then 12 F HCl (50 ml) containing $ZnCl_2$ (10 g) was slowly added. After standing the solution at room temperature for 3 days the product commenced to crystallise and it was collected in crops, washed with 2-propanol and then ether.

The crude product was recrystallised by dissolving it in methanol containing 2 F HCl (20 ml/1 g) and then adding 12 F HCl (5 ml/1 g) containing $ZnCl_2$ (5 g/1 g). The purified product that deposited on cooling to room temperature was collected in fractions, washed and dried as above. The isomeric composition of each fraction of recrystallised product is listed in Table 2.29. The total yield of chloropentaamine complex was 4.85 g or 29.0%.

IX-Chloro(N-cyclohexyl-1,3-propanediamine)(diethylenetriamine) cobalt(III) Tetrabromocadmiumate(II): IX-$[Co(tmd\text{-}hex)(dien)Cl]ZnCl_4$ (0.1 g) was dissolved in 0.2 F CH_3CO_2H at 30° and a solution of 50% HBr (10 ml) containing $CdBr_2.4H_2O$ (2.5 g). The red-purple product crystallised immediately and it was collected, washed with 2-propanol and then ether. The yield was 92.1%.

Table 2.29

Isomeric Composition: Isomers of $[Co(tmd\text{-}hex)(dien)Cl]ZnCl_4$

Crop 1		Crop 2		Crop 3		Crop 4	Crop 5
1	2	1	2	1	2	1	1
0.641**	0.319	0.367	0.919	0.394	0.059	0.716	0.416
(VIII)	(VIII)	(VIII)	(VIII*+IX)	(VIII*+IX)	(VIII)	(VIII+IX)	(VIII)

Crop 6	Crop 7	Crop 8	Crop 9		Crop 10	Crop 11
1	1	1	1	2	1	1
0.457	0.103	0.205	0.025	0.128	0.048	0.052
(IX)	(IX)	(IX)	(IX)	(IX)	(IX)	(IX)

* denotes major component of fraction

** weight in g

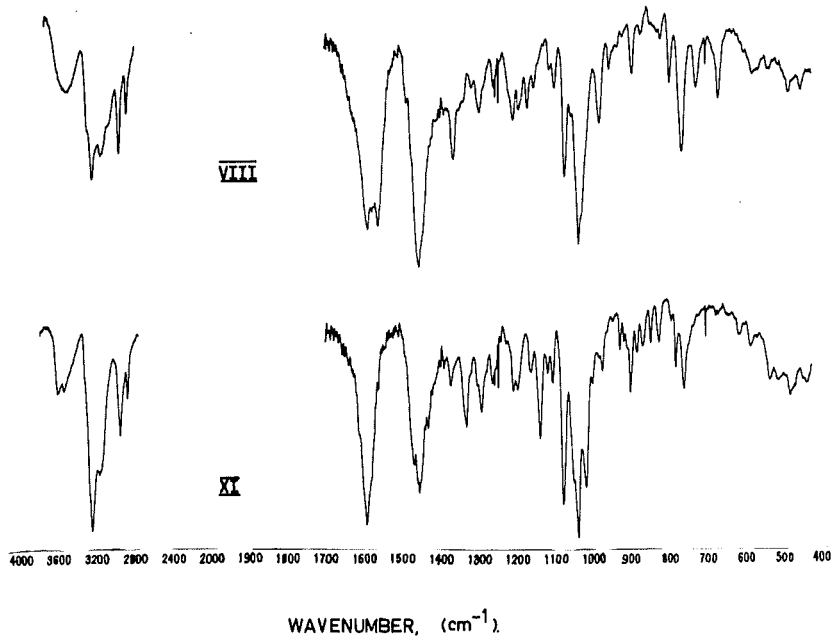
Table 2.30

Analytical Data for [Co(tmd-hex)(dien)Cl]Y

Complex	Calculated				Found			
	C%	H%	Co%	X%[a]	C%	H%	Co%	X%[a]
$[Co(tmd\text{-}hex)(dien)Cl]ZnCl_4$ - VIII	27.83	5.93	10.51	31.60	28.09	5.90	10.53	31.72
$[Co(tmd\text{-}hex)(dien)Cl]ZnCl_4.2H_2O$ - IX	26.15	6.25	9.87	29.69	26.47	6.24	9.89	29.82
$[Co(tmd\text{-}hex)(dien)Cl]CdBr_4.2H_2O$ - IX			7.19	43.31			7.23	42.98

[a] Total halide as found by Ag^+ titration

Figure 2.14 Infrared spectra of VIII and IX - $[Co(tmd\text{-}hex)(dien)Cl]ZnCl_4.xH_2O$ in the range 4000-400 cm^{-1} (KBr Disc).



Attempts to synthesise this salt from the VIII isomer resulted in the formation of an oil.

(C) Complexes of 1,4-diamines with diethyleletriamine

(1) 1,4-butanediamine

Analytical data for the complexes are presented in Table 2.31. The infrared spectra of the chloro $ZnCl_4^{2-}$ isomer is presented in Fig. 2.15.

Isomer of Chloro(1,4-butanediamine)(diethylenetriamine) cobalt(III) Tetrachlorozincate(II): trans-$Co(dien)Cl_3$ (7 g) was suspended in 1:1 methanol/water (100 ml) containing NaOH (2 g) and 1,4-butanediamine (4 ml, 100%) was added. The dark red solution was boiled under reflux for 15 min. and then 12 F HCl (20 ml) containing $ZnCl_2$ (10 g) was slowly added. On standing the solution for 24 hours at room temperature the purple-red crude product began to crystallise. This was collected, washed with 2-propanol and then ether. The crude product was recrystallised by dissolving it in 0.2 F CH_3CO_2H at 50° (0.5 g/20 ml) and then adding 12 F HCl (10 ml/0.5 g) containing $ZnCl_2$ (2.5 g/0.5 g). The purified product that deposited slowly on standing at room temperature was collected in fractions that were washed and dried as above.

Further crops of crude product were obtained on the slow evaporation of the aqueous mother liquor at room temperature and these were recrystallised as above but using a corresponding reduction in the weights and volumes of the reagents used.

The total yield of chloropentaamine product (isomer 1 only) was 2.27 g or 17.3%.

Chloro(1,4-butanediamine)(diethylenetriamine)cobalt(III) Tetrathiocyanatozincate(II): $[Co(1,4\text{-bn})(dien)Cl]ZnCl_4$ (0.25 g) was dissolved in 0.2 F CH_3CO_2H at 35° (25 ml) and NH_4NCS (2.5 g) was added. On standing the solution at room temperature the red salt was slowly deposited and it was collected, washed with ethanol and then air dried. The yield was 71.3%.

(D) Complexes with 1,4,8-triazaoctane

(1) Ethylenediamine

Analytical data for the complexes are presented in Table 2.36. Infrared spectra of the chloro $ZnCl_4^{2-}$ salts are presented in Fig. 2.16.

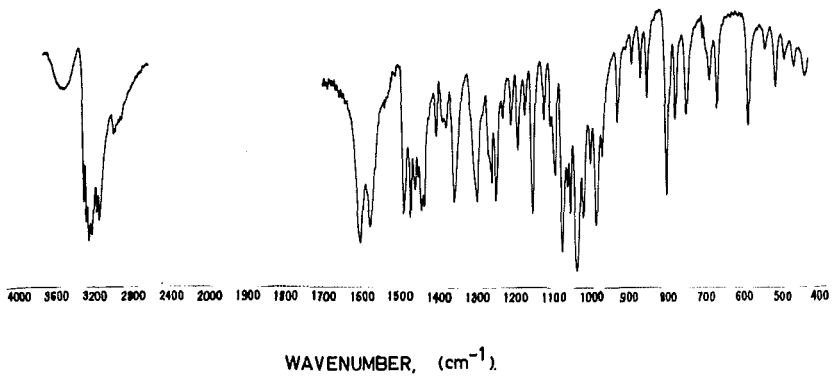
Table 2.31

Analytical Data for [Co(1,4-bn)(dien)Cl]X

Complex	Calculated				Found			
	C%	H%	Co%	X%[a]	C%	H%	Co%	X%[a]
[Co(1,4-bn)(dien)Cl]$ZnCl_4$ - 1	19.49	5.11	11.96	35.96	19.23	5.09	11.92	35.72
[Co(1,4-bn)(dien)Cl]$Zn(NCS)_4$ - 1			10.10	45.89			10.25	45.41

[a] Total halide or NCS^- as found by Ag^+ titration

Figure 2.15 Infrared spectrum of 1 - $[Co(1,4\text{-bn})(dien)Cl]ZnCl_4$ in the region 4000-400 cm^{-1} (KBr Disc).



μ-Peroxobis(ethylenediamine)bis(1,4,8-triazaoctane) dicobalt(III) Perchlorate Dihydrate: An aqueous solution (130 ml) of ethylenediamine (4 g) and 1,4,8-triazaoctane (8 g) was added to a stirred solution of $Co(NO_3)_2.6H_2O$ (20 g) and $NaClO_4.H_2O$ (25 g) in water (250 ml). A rapid stream of O_2 gas was passed through the stirred, room temperature solution and after 30 min., $NaClO_4.H_2O$ (20 g) was added. After a further 90 min. the brown solid material that deposited was collected, washed with 2-propanol and then ether. The yield was 28 g or 87%.

A sample for analysis was prepared by dissolving 2 g of the crude material in water at 50° (40 ml) and then adding $NaClO_4.H_2O$ (12 g). The purified product that was immediately deposited was collected, washed and dried as above. A 95% recovery was obtained.

Isomers of Chloro(ethylenediamine)(1,4,8-triazaoctane) cobalt(III) Tetrachlorozincate(II):

Method A: $[Co_2(en)_2(2,3\text{-tri})_2O_2](ClO_4)_4.2H_2O$ (10 g) was added to a solution of 12 F HCl (30 ml) in water (55 ml) containing $ZnCl_2$ (12 g). The solution was heated on a steam bath (ca. 80°) until the effervescence ceased (45 min.), during which time a red crystalline material was deposited. After heating for a further 15 min., the crude product was collected from the hot solution and was washed

with 2-propanol and then ether. The crude product was recrystallised by dissolving it in 0.2 F HCl (1 g/35 ml) at 80° and then adding 12 F HCl (5 ml/1 g) containing $ZnCl_2$ (2 g/1 g). The purified product that deposited on cooling the solution to room temperature was collected in fractions and was washed and dried as above.

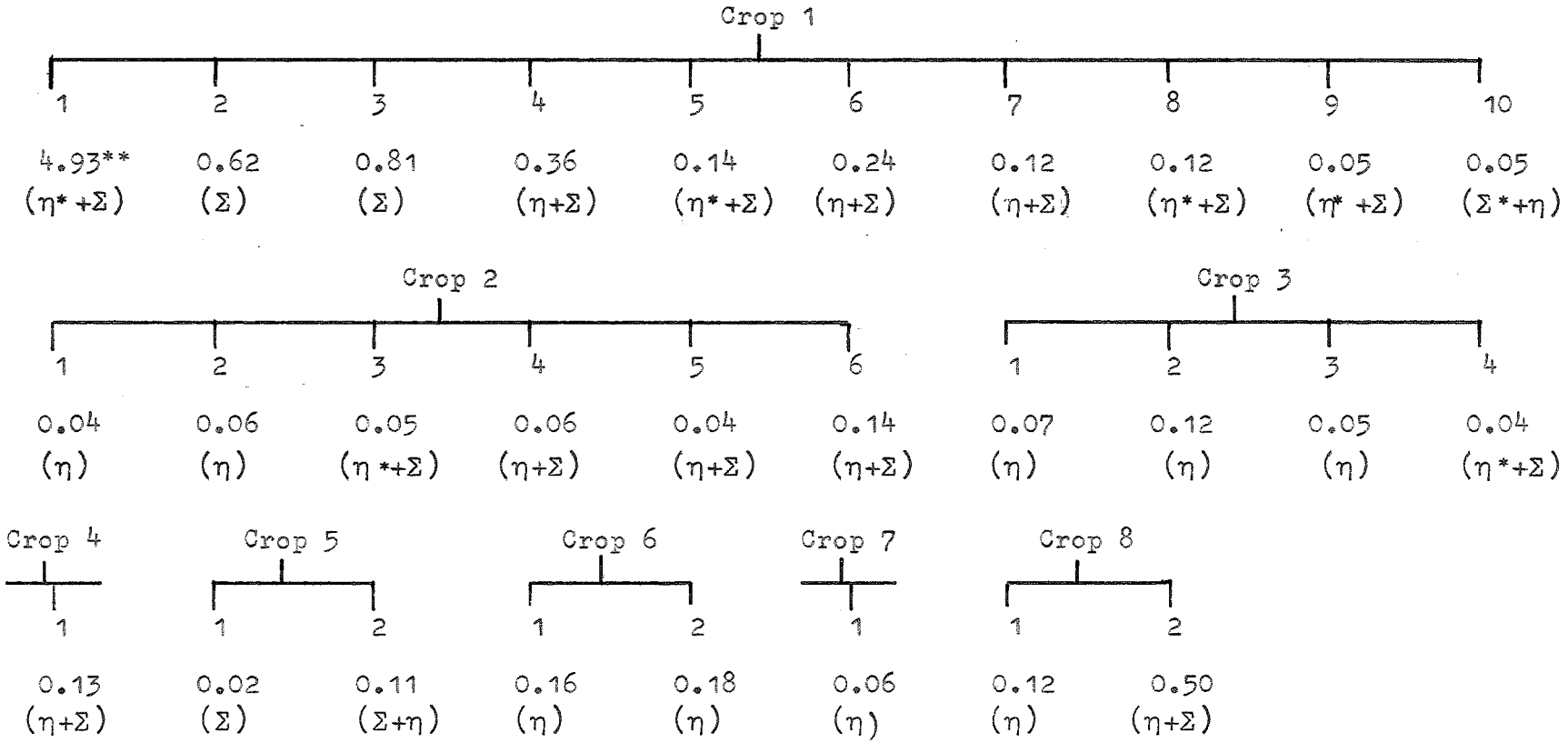
Further crude product was obtained on the slow evaporation of the aqueous mother liquor at room temperature (final volume 70 ml). These were recrystallised as above but using a corresponding reduction in the volumes and weights of the reagents used.

The total yield of chloropentaamine complex was 9.39 g or 92.2%. The isomeric composition of each fraction of recrystallised product are listed in Table 2.32.

Method B: trans-Co(2,3-tri)$(NO_2)_3$ (14 g) was suspended in water (30 ml) and ethylenediamine (3.3 ml, 100%) was added. The solution was stirred and allowed to digest the neutral complex on a steam bath at ca. 80°. After one hour, the dark brown solution was cooled in ice and 12 F HCl (15 ml) was slowly added. The solution was reheated for a further 30 min. and then $ZnCl_2$ (10 g) was added. After a further one hour at ca. 80° the crude product commenced to crystallise and it was collected in crops, washed with 2-propanol and then ether. The crude product was recrystallised by dissolving it in 0.2 F HCl at 80°

Table 2.32

Isomeric Composition of fractions of $[Co(2,3\text{-tri})(en)Cl]ZnCl_4$; Method A



* denotes major component of fraction

** weight in g

(1 g/50 ml) and then adding 12 F HCl (5 ml/1 g) containing $ZnCl_2$ (2 g/1 g). The purified product that was deposited on cooling to room temperature was collected in fractions and was washed and dried as above.

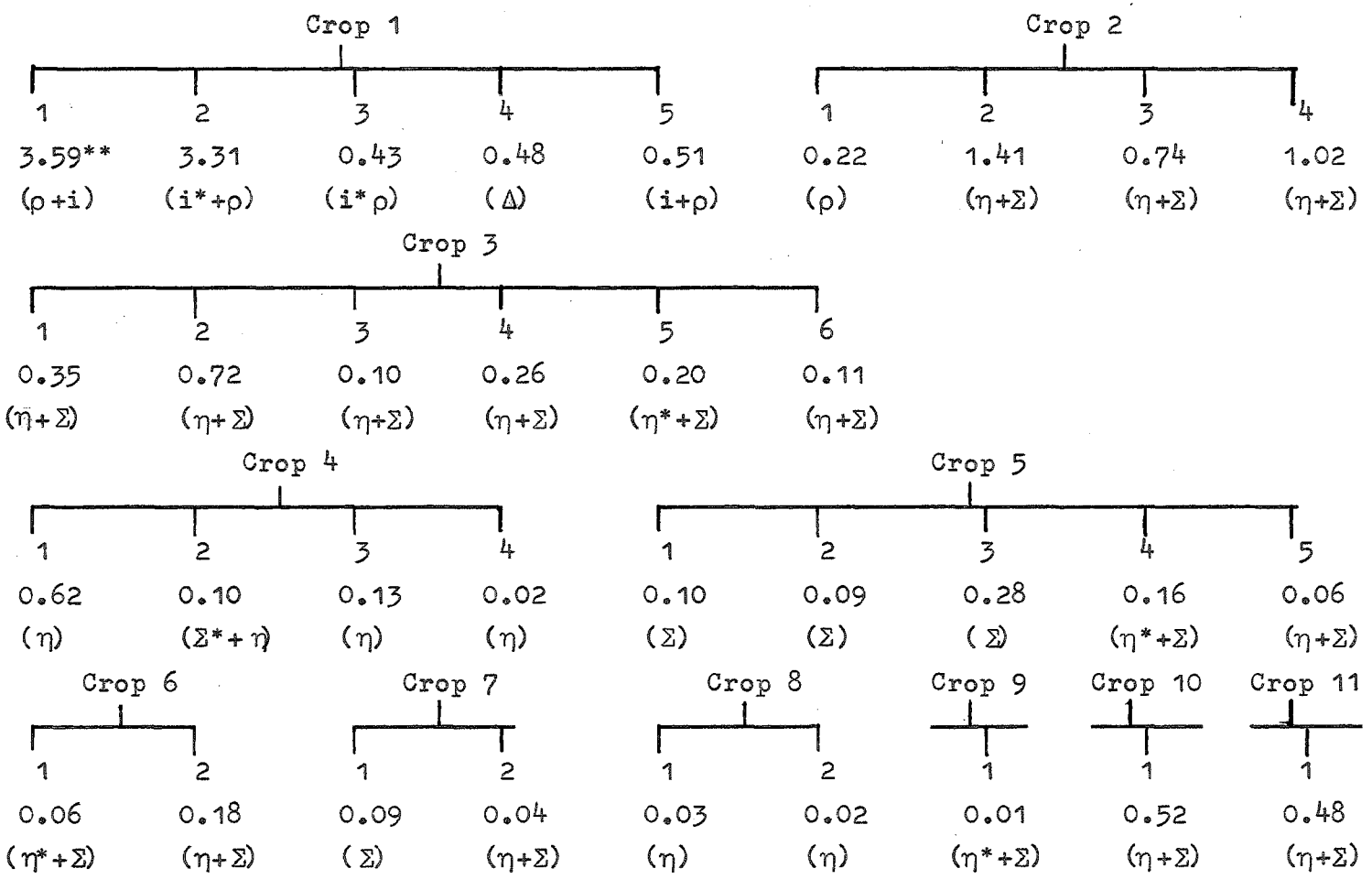
The aqueous mother liquor deposited further crops on slow evaporation at room temperature. These were recrystallised as above but using a corresponding reduction in the weights and volumes of the reagents used.

The total yield of chloropentaamine complex was 15.44 g or 67.3%. The isomeric composition of each fraction of recrystallised product are listed in Table 2.33.

Method C: trans-$Co(2,3\text{-tri})(NO_2)_3$ (10 g) was suspended in water (22.5 ml) and ethylenediamine (2.8 ml, 100%) was added. The mixture was heated on a steam bath (ca. 80°) for 30 min. during which time the neutral complex dissolved to give a dark brown solution. 12 F HCl (30 ml) was cautiously added and the solution was reheated for a further three hours during which time a dark red colour was formed. $ZnCl_2$ (10 g) was then added and the crystalline product that deposited immediately was collected in crops washed with 2-propanol and then ether. The crude product was recrystallised by dissolving it in 0.2 F CH_3CO_2H at 80° (1 g/25 ml) and then adding 12 F HCl (5 ml/1 g) containing $ZnCl_2$ (2.5 g/1 g). The purified product that deposited on cooling the solution to room temperature was collected in fractions, washed and dried as above.

Table 2.33

Isomeric Compositions of fractions of $[Co(2,3\text{-tri})(en)Cl]ZnCl_4$; Method B



* denotes major component of fraction

** weight in g

Further crops of crude product were obtained from the aqueous mother liquor on slow evaporation at room temperature. These were recrystallised as above but using a corresponding reduction in the weights and volumes of the reagents used.

The total yield of chloropentaamine complex was 8.27 g or 47.1%. The isomeric composition of each fraction of recrystallised product is listed in Table 2.34.

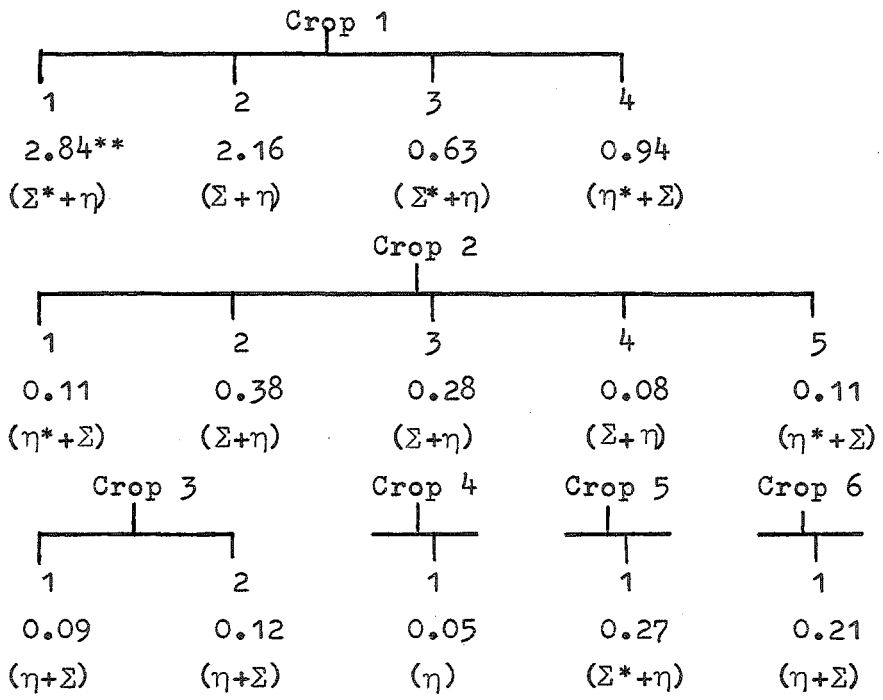
Qualitative Isomerisation Reactions: Small quantities of the pure isomers were taken and subjected to the following chemical reactions. The isomeric composition of the chloro $ZnCl_4^{2-}$ and the nitro $ZnCl_4^{2-}$ salts was determined by examination of the infrared spectrum.

(a) Reaction with Nitrous Acid: Nitro compounds derived from the η, Σ, "ρ", "*i*" and "Δ" isomers of $[Co(2,3\text{-tri})(en)Cl]ZnCl_4.xH_2O$ were prepared using the method described later. The products were decomposed by heating a solution of each in 3 F HCl on a steam bath (ca. 80°) for 1 hour. The $ZnCl_4^{2-}$ salts of the chloro isomers generated in this manner were deposited by the addition of $ZnCl_2$. The transformations that resulted were: η → η+Σ; Σ → Σ; "ρ" → η+Σ; "*i*" → Σ; "Δ" → η+Σ.

(b) Base Hydrolysis: The η, Σ, "ρ", "*i*" and "Δ" isomers of $[Co(2,3\text{-tri})(en)Cl]ZnCl_4.xH_2O$ were separately dissolved in water (0.25 g/10 ml) and 1 F NaOH (10 ml) was added.

Table 2.34

Isomeric Compositions of fractions of $[Co(2,3\text{-tri})(en)Cl]ZnCl_4$; Method C



* denotes major component(s) of fraction

** weight in g

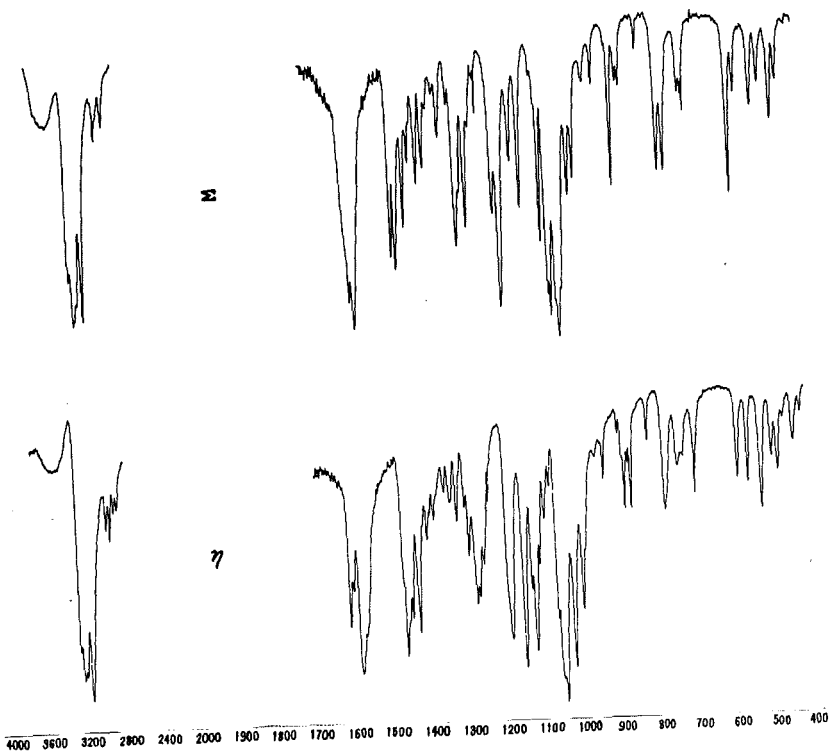


Figure 2.16 Infrared spectra of α and η - $[Co(2,3\text{-tri})(en)Cl]ZnCl_4$ in the region 4000-400 cm-1 (KBr Disc).

The solutions were heated at 70° for 20 min. and then 12 F HCl (10 ml) containing $ZnCl_2$ (3 g) was added. The solutions were left to stand at room temperature overnight and the product that deposited slowly was collected, washed with 2-propanol and then ether. The results were: η → Σ; Σ → Σ; "ρ" → Σ; "*i*" → Σ; "Δ" → Σ.

Σ-Chloro(ethylenediamine)(1,4,8-triazaoctane)cobalt(III) Tetrabromozincate(II): Σ-[Co(2,3-tri)(en)Cl]$ZnCl_4$ (0.2 g) was dissolved in 0.2 F CH_3CO_2H (12 ml) at 60° and a solution of 63% HBr (5 ml) containing $ZnBr_2$ (1 g) was added. The crystalline product that deposited on cooling the solution to room temperature was collected from the ice cooled solution and was washed with 2-propanol and then ether. The yield was 92.7%.

η-Chloro(ethylenediamine)(1,4,8-triazaoctane)cobalt(III) Tetrabromocadmiumate(II): η-[Co(2,3-tri)(en)Cl]$ZnCl_4$ (0.5 g) was dissolved in 0.2 F CH_3CO_2H (30 ml) at 40° and a solution of 30% HBr (40 ml) containing $CdBr_2.4H_2O$ (5 g) was added. The purple-red crystalline product that was immediately deposited was collected from the ice cooled solution and was washed with 2-propanol and then ether. The yield was 90.3%.

Σ-Chloro(ethylenediamine)(1,4,8-triazaoctane)cobalt(III) Tetrathiocyanatozincate(II): Σ-[Co(2,3-tri)(en)Cl]$ZnCl_4$ (0.25 g) was dissolved in 0.2 F CH_3CO_2H at 60° (40 ml) and NH_4NCS (3 g) dissolved in water (5 ml) containing $Zn(O_2CCH_3)_2$ (1 g) was added. After standing the solution at room temperature for two days the red crystalline product was collected, washed with 2-propanol and then air dried. The yield was 79.3%.

Isomers of Bromo(ethylenediamine)(1,4,8-triazaoctane) cobalt(III) Tetrabromozincate(II): $[Co_2(en)_2(2,3\text{-tri})_2O_2](ClO_4)_4.2H_2O$ (3 g) was added to 20% HBr (30 ml) containing $ZnBr_2$ (3 g). The solution was heated on a steam bath (ca. 80°) and the purple product, that commenced to crystallise after 15 min., was collected in crops and was washed with 2-propanol and then ether. The crude product was recrystallised by dissolving it in 0.2 F CH_3CO_2H at 60° (1 g/60 ml) and then adding 63% HBr (5 ml/1 g) containing $ZnBr_2$ (3 g/1 g). The purified product that deposited on cooling the solution to room temperature was collected in fractions, washed and dried as above.

Further crops of crude product were obtained from the aqueous mother liquor on slow evaporation at room temperature and these were recrystallised as above but using a corresponding reduction in the weights and volumes of the reagents used.

The total yield of bromopentaamine complex was 2.61 g or 58.4%. The isomeric composition of each fraction of recrystallised product is listed in Table 2.35.

The η and Σ isomer products were separated by the following procedure: (η+Σ)-[Co(2,3-tri)(en)Br]$ZnBr_4$ (0.5 g) was dissolved in 0.1 F $HClO_4$ (20 ml) at 40° and $NaClO_4.H_2O$ (8 g) was added. On cooling the solution to room temperature the product that deposited slowly was collected in crops, washed with 2-propanol and then ether. The perchlorate salts were converted to the tetrabromozincate(II) salts by dissolving each crop in 0.2 F CH_3CO_2H at 30° (0.1 g/10 ml) and then adding 63% HBr (5 ml/0.1 g) containing $ZnBr_2$ (2.5 g/0.1 g). The purified product that deposited was collected, washed and dried as above. The composition of each crop was:

Crop Number	Composition
1	Σ
2	Σ
3	η

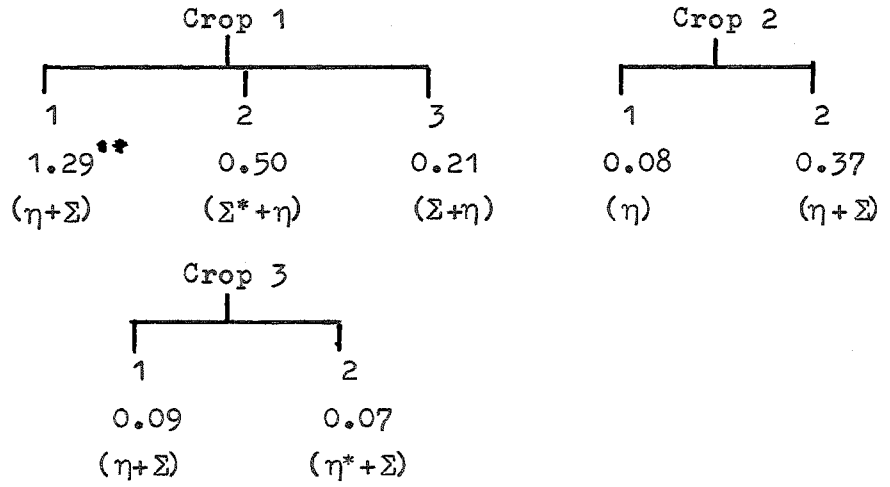
A 77% recovery was obtained.

η-Iodo(ethylenediamine)(1,4,8-triazaoctane)cobalt(III) Tetrachlorozincate(II):

Method A: $[Co_2(en)_2(2,3\text{-tri})_2O_2](ClO_4)_4.2H_2O$ (5 g) was suspended in 3 F $HClO_4$ (25 ml) and NaI (10 g) was added.

Table 2.35

Isomeric Composition of fractions of $[Co(2,3\text{-tri})(en)Br]ZnBr_4$



* denotes major component(s) of fraction

** weight in g

The mixture was heated at 60° for 20 min. and then a further portion of NaI (10 g) was added. After cooling to room temperature the brown precipitate was collected, washed with acetone, until the residue was green, and then with ether. The crude product was purified dissolving it in 0.2 F CH_3CO_2H (0.1 g/25 ml) at 50° and then adding 12 F HCl (5 ml/0.1 g) containing $ZnCl_2$ (2.5 g/0.1 g). The product, that was immediately deposited, was collected, washed with 2-propanol and then ether. The yield was 3.7%.

Method B: A mixture of the η and Σ isomers of $[Co(2,3\text{-tri})(en)Cl]ZnCl_4$ (1 g) was dissolved in water (10 ml) and NaI (2.5 g) was added. The solution was boiled under reflux for 30 min. and then NaI (2.5 g) was added. On standing the solution at room temperature for 2 days, the brown material that deposited was collected and washed with acetone until the residue became green. The crude product was purified by dissolving it in water (0.1 g/30 ml) and then adding 12 F HCl (10 ml/0.1 g) containing $ZnCl_2$ (2.5 g/0.1 g). The purified product that deposited immediately was collected, washed with 2-propanol and then ether. The yield was 23.4%.

η and Σ-Nitro(ethylenediamine)(1,4,8-triazaoctane)cobalt (III) Tetrachlorozincate(II): The η and Σ isomers of $[Co(2,3\text{-tri})(en)Cl]ZnCl_4$ (0.25 g) were separately dissolved in 0.2 F HCl (10 ml) and $NaNO_2$ (1 g) was added. The

solutions were heated on a steam bath (ca. 80°) for 15 min. during which time the mild effervescence ceased and the colour changed from red to orange. The hot solutions were slowly poured into 1:1 2-propanol/acetone (25 ml) containing 12 F HCl (1 ml) and $ZnCl_2$ (1 g). The yellow crystalline products, that deposited on cooling the solutions to room temperature, were collected, washed with acetone and then ether. The yields were η 51.3% and Σ 72.0%. The first crop derived from the η isomer was the pure Σ isomer.

(E) Complexes of 1,2-diamines with dipropylenetriamine

(1) Ethylenediamine

Complexes of this system have already been reported[30]. However, the reaction between ethylenediamine and trans-$Co(dpt)(NO_2)_3$ was not reported in that publication. Infrared spectra of the chloro $ZnCl_4^{2-}$ salts in the region 1700-400 cm^{-2} are presented in Figure 3, reference 30.

Isomers of Chloro(ethylenediamine)(dipropylenetriamine) cobalt(III) Tetrachlorozincate(II): trans-$Co(dpt)(NO_2)_3$ (14 g) was suspended in water (30 ml) and ethylenediamine (3.9 ml, 100%) was added. The solution was gently heated at 50° for 45 min. during which time the neutral complex dissolved to give a dark brown solution. 12 F HCl (15 ml) was slowly added to the ice cooled solution and then it

Table 2.36

Analytical Data for [Co(2,3-tri)(en)X]Y

Complex	Calculated				Found			
	C%	H%	Co%	X%[a]	C%	H%	Co%	X%[a]
$[Co_2(2,3\text{-tri})_2(en)_2O_2](ClO_4)_4 \cdot 2H_2O$	17.92	5.37	12.56		18.06	5.11	12.67	
$[Co(2,3\text{-tri})(en)Cl]ZnCl_4$ - Σ	17.56	4.84	12.31	37.02	17.84	4.81	12.21	36.89
- η					17.90	4.81	12.25	36.92
$[Co(2,3\text{-tri})(en)Cl]ZnBr_4$ - Σ			8.79	54.07			8.62	53.87
$[Co(2,3\text{-tri})(en)Cl]CdBr_4$ - η			8.38	50.46			8.31	50.37
$[Co(2,3\text{-tri})(en)Cl]Zn(NCS)_4$ - Σ			10.35	47.04			10.28	47.12
$[Co(2,3\text{-tri})(en)Br]ZnBr_4$ - Σ			8.41	56.98			8.35	56.87
- η							8.32	56.89
$[Co(2,3\text{-tri})(en)I]ZnCl_4$ - η			10.33	47.11			10.25	46.93
$[Co(2,3\text{-tri})(en)NO_2]ZnCl_4$ - Σ			12.04	28.98			12.08	28.91
- η							12.01	28.88

[a] Total halide and thiocyanate as found by Ag^+ titration

was heated at 80° for two hours. $ZnCl_2$ (10 g) was then added and the red product that deposited was collected in crops, washed with 2-propanol and then ether. The crude product was recrystallised by dissolving it in 0.2 F CH_3CO_2H (1 g/60 ml) and then adding 12 F HCl (25 ml/1 g) containing $ZnCl_2$ (2.5 g/1 g). The purified product that deposited on cooling the solution to room temperature was collected in fractions, washed and dried as above.

On slow evaporation of the aqueous mother liquor at room temperature, further crops of crude product were obtained and these were recrystallised as above but using a corresponding reduction in the weights and volumes of the reagents used.

The total yield of chloropentaamine complex was 3.13 g or 13.4%. The isomeric composition of each fraction of recrystallised product is listed in Table 2.37.

(2) 1,2-propanediamine

Analytical data for the complexes are presented in Table 2.41. Infrared spectra of the chloro $ZnCl_4^{2-}$ salts are presented in Fig. 2.17.

Isomers of Chloro(1,2-propanediamine)(dipropylenetriamine) cobalt(III) Tetrachlorozincate(II):

Method A: An aqueous solution (100 ml) of 1,2-propanediamine (3.1 g) and dipropylenetriamine (6.6 g) was added to a

Table 2.37

Isomeric Composition of fractions of $[Co(en)(dpt)Cl]ZnCl_4$

Crop 1	Crop 2	Crop 3			Crop 4
1	1	1	2	3	1
0.50**	1.07	0.40	0.27	0.05	0.37
(α)	(β*+α)	(β*+α)	(β*+α)	(β+α)	(β)

Crop 5	Crop 6	Crop 7	Crop 8	Crop 9	Crop 10
1	1	1	1	1	1
0.03	0.08	0.08	0.04	0.14	0.10
(β)	(β)	(β)	(β)	(β)	(β)

* denotes major component of fraction

** weight in g

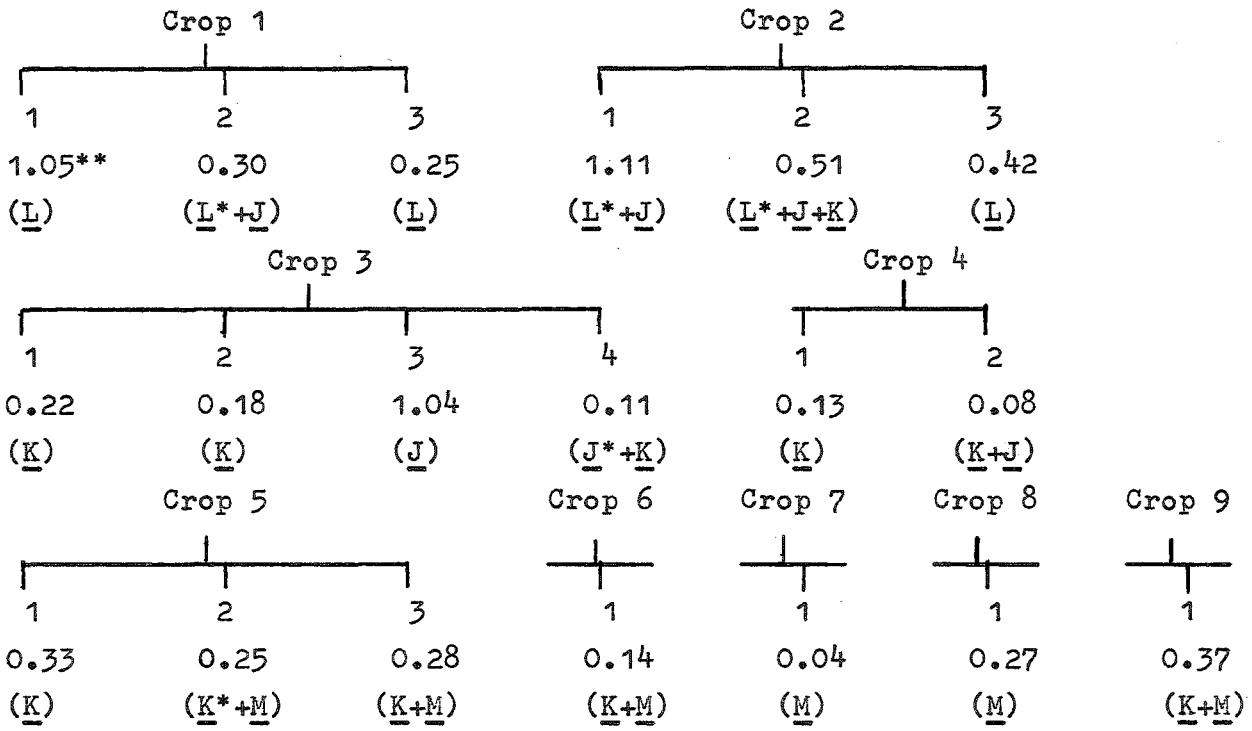
stirred solution of $Co(NO_3)_2.6H_2O$ (15 g) and $NaClO_4.H_2O$ (15 g) in water (200 ml). A rapid stream of O_2 gas was passed through the stirred, room temperature solution and after 45 min., $NaClO_4.H_2O$ (10 g) was added. After a further one hour, the brown oil that was formed was separated by decanting off the aqueous mother liquor. 6 F HCl (120 ml) containing $ZnCl_2$ (25 g) was added to the oil and the mixture was heated on a steam bath (ca. 80°) until the effervescence ceased (ca. 1 hour), during which time the mauve-pink crude L isomer was deposited. The crude product was collected, washed with 2-propanol and then ether. The crude product was recrystallised by dissolving it in 0.2 F CH_3CO_2H (1 g/20 ml) at 60° and then adding 12 F HCl (5 ml/1 g) containing $ZnCl_2$ (2.5 g/1 g). The purified product, that deposited on cooling the solution to room temperature, was collected in fractions, washed and dried as above.

The aqueous mother liquor yielded further crops of crude product on slow evaporation at room temperature. These were recrystallised as above, but using a corresponding reduction in the weights and volumes of the reagents used.

The total yield of chloropentaamine product was 7.11 g or 27.3%. The isomeric compositions of the fractions of recrystallised product are tabulated in Table 2.38.

Table 2.38

Isomeric Composition of fractions $[Co(pn)(dpt)Cl]ZnCl_4$; Method A



* denotes major component(s) of fraction

** weight in g

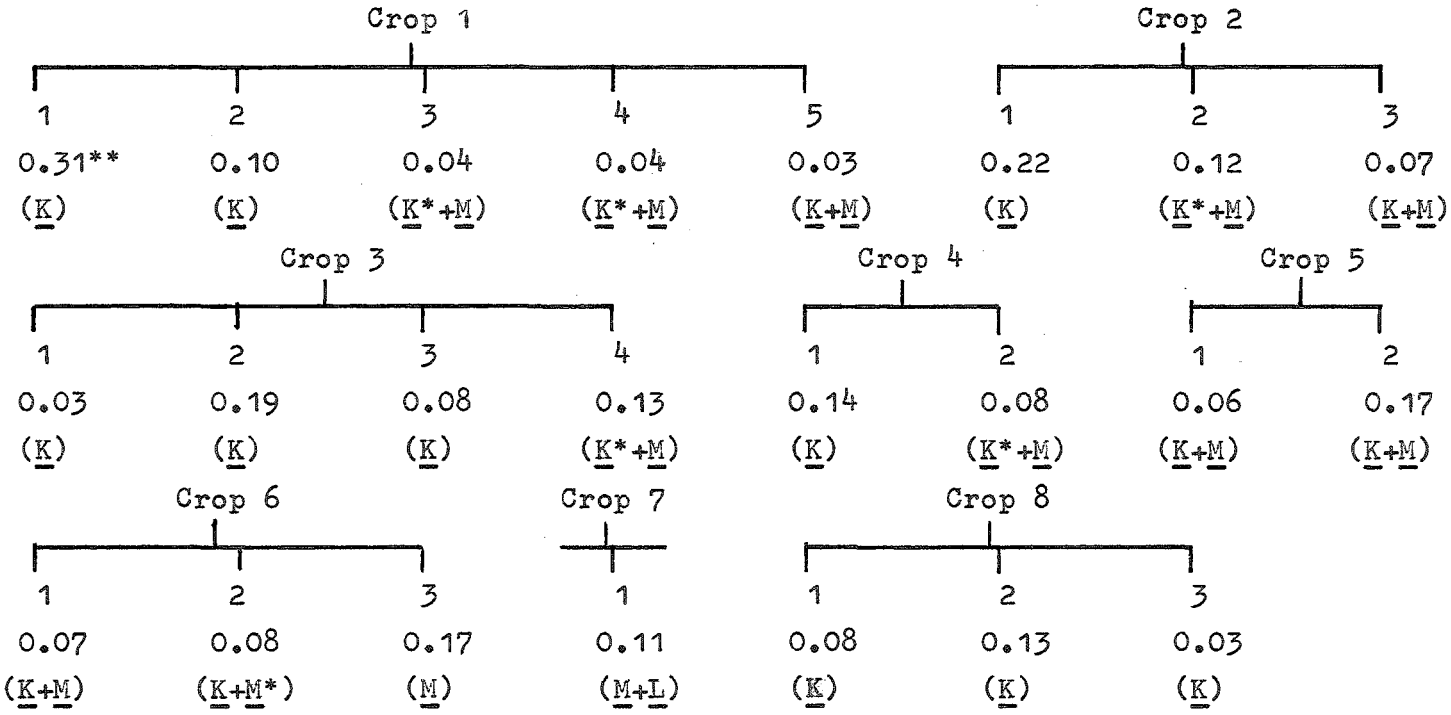
Method B: trans-$Co(dpt)(NO_2)_3$ (14 g) was suspended in water (30 ml) and 1,2-propanediamine (4.0 ml, 100%) was added. The mixture was heated on a steam bath (ca. 80°) for one hour during which time the neutral complex dissolved to form a dark brown solution. The solution was cooled in an ice bath and then 12 F HCl (15 ml) containing $ZnCl_2$ (10 g) was added cautiously. The solution was reheated for a further three hours during which time the evolution of oxide of nitrogen ceased, and a violet product was slowly deposited. The crude product was collected, washed with 2-propanol and then ether. It was recrystallised by dissolving it in 0.2 F CH_3CO_2H (0.5 g/15 ml) at 40° and then adding 12 F HCl (5 ml/0.5 g) containing $ZnCl_2$ (2.5 g/0.5 g). The purified product that deposited on cooling to room temperature was collected in fractions, washed and dried as above.

The aqueous mother liquor deposited further crops of crude product on slow evaporation at room temperature and these were recrystallised as above but using a corresponding reduction in the weights and volumes of the reagents used.

The total yield of chloropentaamine product was 2.48 g or 11.6%. The isomeric compositions of the fractions of recrystallised product are tabulated in Table 2.39.

Table 2.39

Isomeric composition of fractions of $[Co(pn)(dpt)Cl]ZnCl_4$; Method B



* denotes major component of fraction

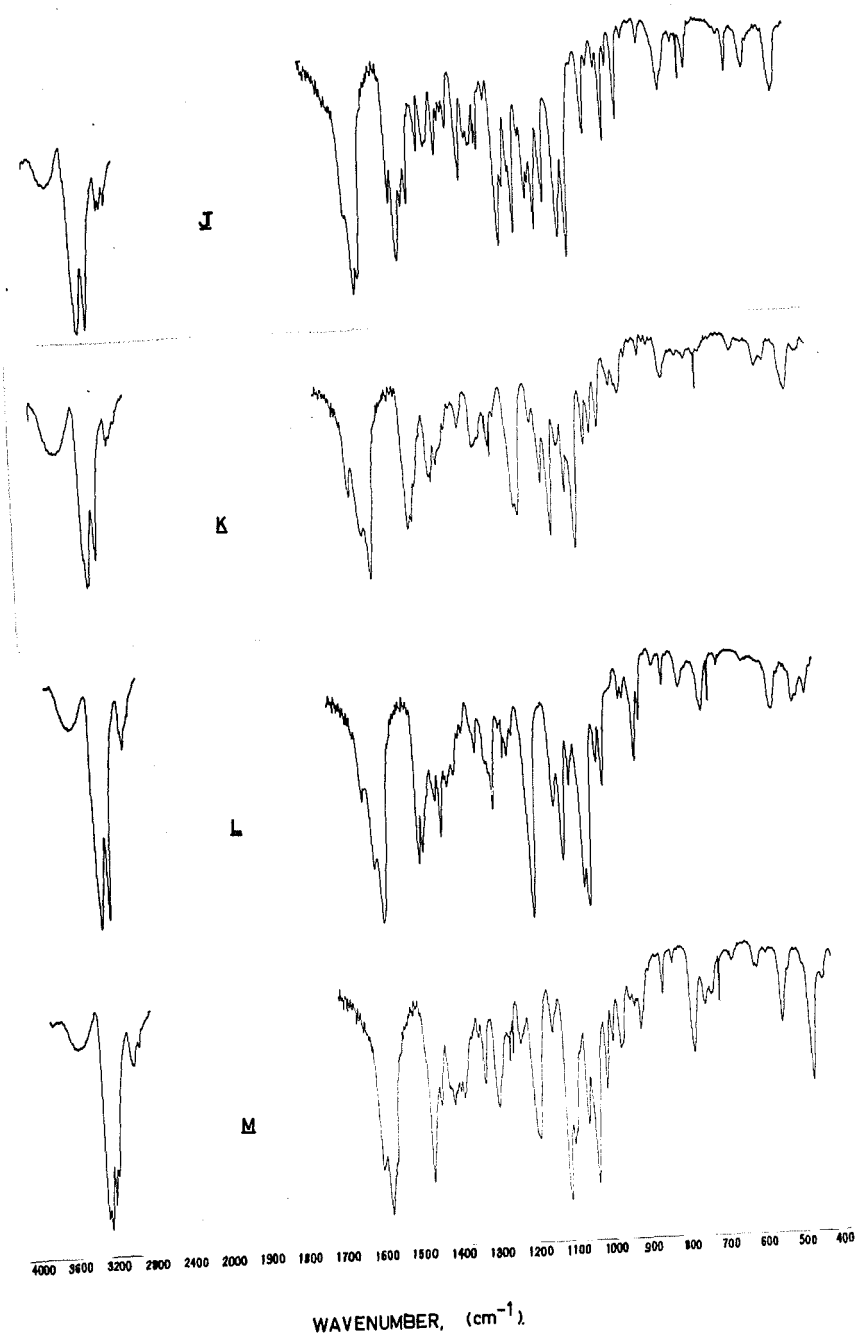
** weight in g

Qualitative Isomerisation Reactions: Small quantities of the pure isomers were taken and subjected to the following chemical reactions. The isomeric composition of the chloro $ZnCl_4^{2-}$ and the nitro $ZnCl_4^{2-}$ salts was determined by examination of the infrared spectrum.

(a) Reaction with Nitrous Acid: Nitro compounds derived from the J, K, L and M isomers of $[Co(pn)(dpt)Cl]ZnCl_4$ were prepared by the method described later. The products were decomposed by heating a solution of each in 3 F HCl on a steam bath (ca. 80°) for 1 hour. The $ZnCl_4^{2-}$ salts of the chloro isomers generated in this manner were deposited by the addition of $ZnCl_2$. The transformations that resulted were: J → J+M; K → K; L → L+K; M → M.

(b) Base Hydrolysis: The J, K, L and M isomers of $[Co(pn)(dpt)Cl]ZnCl_4$ were separately dissolved in water (0.25 g/10 ml) and 1 F NaOH (10 ml) was added. The solutions were heated at 60° for 20 min. and then 12 F HCl (10 ml) containing $ZnCl_2$ (4 g) was added. The solutions were left to stand at room temperature for three days and the product was collected, washed with 2-propanol and then ether. The results were: J → J, K → L, L → L, M → J.

Figure 2.17 Infrared spectra of J, K, L and M - $[Co(pn)(dpt)Cl]ZnCl_4$ in the range 4000-400 cm^{-1} (KBr Disc).



L-Chloro(1,2-propanediamine)(dipropylenetriamine)cobalt(III) Perchlorate: L-[Co(pn)(dpt)Cl]$ZnCl_4$ (0.5 g) was dissolved in 3 F $HClO_4$ (20 ml) at 40° and $NaClO_4.H_2O$ (5g) was added. The crystalline product that was slowly deposited from the ice cooled solution was collected, washed with 2-propanol and then ether. The yield was 45%.

J, K, L and M-Chloro(1,2-propanediamine)(dipropylenetriamine) cobalt(III) Tetrabromocadmiumate(II): The J, K, L and M isomers of [Co(pn)(dpt)Cl]$ZnCl_4$ were separately dissolved in 0.2 F CH_3CO_2H (0.1 g/10 ml, 0.1 g/15 ml, 0.15 g/10 ml, 0.1 g/10 ml respectively) and a solution of 50% HBr (10 ml, 10 ml, 15 ml, 10 ml) containing $CdBr_2.4H_2O$ (2 g, 2.5 g, 2.5 g, 2 g) was added. The crystalline products were deposited on standing the solutions at room temperature. The products were collected from the ice cooled solutions, washed with 2-propanol and then ether. The yields were J 67.2%, K 69.8%, L 84.5% and M 71.2%.

L, K and M-Bromo(1,2-propanediamine)(dipropylenetriamine) cobalt(III) Tetrabromozincate(II): An aqueous solution (100 ml) of 1,2-propanediamine (3.1 g) and dipropylene-triamine (5.2 g) was added to a stirred solution of $CoCl_2.6H_2O$ (10 g) and $NaClO_4.H_2O$ (15 g) in water (150 ml). A rapid stream of O_2 gas was passed through the stirred, room temperature solution and after 45 min., $NaClO_4.H_2O$

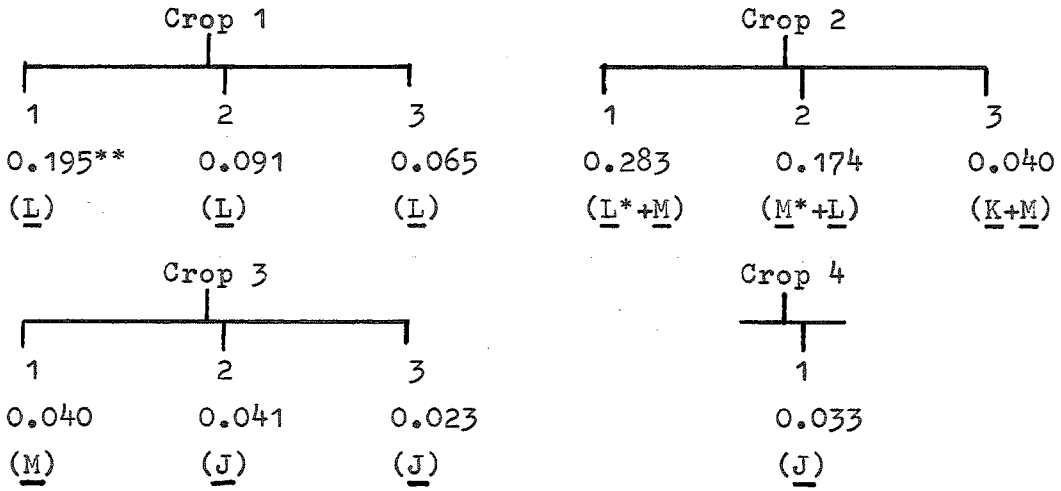
(10 g) was added. The aqueous mother liquor was decanted from the residual brown oil of peroxo complex. 30% HBr (150 ml) was added to the oil and the solution was then heated on a steam bath (ca. 80°) for one hour. $ZnBr_2$ (10 g) was then added and the solution was heated for a further one hour. On cooling the solution to room temperature, the crude product was slowly deposited and it was collected in crops, washed with 2-propanol and then ether. The crude product was recrystallised by dissolving it in 0.2 F CH_3CO_2H at 60° (0.5 g/40 ml) and then adding 50% HBr (15 ml/0.5 g) containing $ZnBr_2$ (2.5 g/0.5 g). The purified product, that deposited on cooling to room temperature, was collected in fractions, washed and dried as above.

The aqueous mother liquor was reheated to 80° to evaporate it to ca. 100 ml. 50% HBr (20 ml) was then added to the solution and a further crop of crude complex was slowly obtained on cooling the solution to room temperature. This was recrystallised as above but using a corresponding reduction in the volumes and weights of the reagents used.

The total yield of bromopentaamine product was only 0.99g or 3.3%. The isomeric composition of each fraction of recrystallised product is listed in Table 2.40.

Table 2.40

Isomeric Compositions: $[Co(pn)(dpt)Br]ZnBr_4$



* denotes major component of fraction

** weight in g

J, M-Bromo(1,2-propanediamine)(dipropylenetriamine)cobalt (III) Tetrabromozincate(II): J-[Co(pn)(dpt)Cl]$ZnCl_4$ (0.25 g) was dissolved in water (15 ml) and 50% HBr (5 ml) was added. The solution was boiled under reflux for 20 min. during which time there was a rapid colour change from mauve-red to purple. The hot solution was poured into 50% HBr (15 ml) containing $ZnBr_2$ (3 g). The purple product, that was deposited in crops on cooling the solution to room temperature was collected, washed with 2-propanol and then ether. The isomeric composition of the crops was:

Crop No.	Weight(g)	Isomeric Composition
1	0.069	J
2	0.059	J
3	0.087	M + J
4	0.035	M

The total yield of bromopentaamine complex was 0.250 g or 65.7%.

L and K-Bromo(1,2-propanediamine)(dipropylenetriamine) cobalt(III) Tetrabromocadmiumate(II): K-[Co(pn)(dpt)Cl] $ZnCl_4$ (0.25 g) was dissolved in water (15 ml) and 50% HBr (5 ml) was added. The solution was boiled under reflux for 20 min. The hot solution was then poured into 50% HBr (10 ml) containing $CdBr_2.4H_2O$ (5 g). On cooling the

solution to room temperature the product, that was slowly deposited, was collected in crops, washed with 2-propanol and then ether. The isomeric composition of the crops was

Crop No.	Weight(g)	Isomeric Composition
1	0.063	L
2	0.053	L + K
3	0.071	K
4	0.027	K
5	0.064	K

The total yield of bromopentaamine complex was 0.288 g or 70.1%.

J, K, L and M-Nitro(1,2-propanediamine)(dipropylenetriamine) cobalt(III) Tetrachlorozincate(II): The J, K, L and M isomers of $[Co(pn)(dpt)Cl]ZnCl_4$ were separately dissolved in 0.1 F HCl (0.1 g/5 ml, 0.15 g/10 ml, 2 g/50 ml, 0.1 g/10 ml respectively) and $NaNO_2$ (0.5 g, 1 g, 6 g, 0.5 g)was added. The solutions were heated on a steam bath (ca. 80°) for 15 min. during which time there was mild effervescence and the colour changed from mauve-red to orange. The hot solutions were slowly poured into 1:1 2-propanol/acetone (25 ml, 25 ml, 200 ml, 25 ml) containing 12 F HCl (0.25 ml, 0.5 ml, 1 ml, 0.25 ml) and $ZnCl_2$ (1 g, 2 g, 5 g, 1 g). On cooling the solutions to room temperature, the orange-yellow crystalline products were deposited and these were

collected, washed with acetone and then ether. The yields were J 59.4%, K 56.7%, L 72.3% and M 64.9%.

The second crops derived from the J and L isomers contained the M and K isomers respectively.

(3) Isobutylenediamine

Analytical data for the complexes are presented in Table 2.44. Infrared spectra of the chloro $ZnCl_4^{2-}$ salts are presented in Fig. 2.18.

Isomers of Chloro(isobutylenediamine)(dipropylenetriamine) cobalt(III) Tetrachlorozimcate(II):

Method A: An aqueous solution (200 ml) of isobutylenediamine (8 ml) and dipropylenetriamine (14 ml) was added to a stirred solution of $Co(NO_3)_2.6H_2O$ (30 g) in water (400 ml). A rapid stream of O_2 gas was passed through the stirred, room temperature for two hours. $NaClO_4.H_2O$ (90 g) was added and the brown oil that formed was separated by decantation. 4 F HCl (100 ml) was added to the residual oil (ca. 10 g) and the solution was heated on a steam bath at ca. 80° until the effervescence ceased (15 min.) and then $ZnCl_2$ (20 g) was added. After heating for a further one hour, the purple crystalline material that deposited was collected in fractions, washed with 2-propanol and then ether. The crude product was recrystallised by dissolving it in 0.2 F

Table 2.41

Analytical Data for [Co(pn)(dpt)X]Y

Complex	Calculated					Found				
	C%	H%	N%	Co%	X%[a]	C%	H%	N%	Co%	X%[a]
$[Co(pn)(dpt)Cl]ZnCl_4$ - J	21.32	5.37	13.82	11.63	34.97	21.19	5.37	13.55	11.57	34.75
- K						21.52	5.37		11.50	34.80
- L						21.70	5.41	13.50	11.55	34.81
- M						21.59	5.45		11.52	34.75
$[Co(pn)(dpt)Cl]CdBr_4$ - J				8.05	48.52				8.07	48.65
- K									8.02	48.63
- L									8.08	48.47
- M									8.08	48.51
$[Co(pn)(dpt)Cl](ClO_4)_2$ - L				11.82	7.11				11.85	7.10
$[Co(pn)(dpt)Br]ZnBr_4$ - J	14.82	3.73		8.08	54.79	15.13	3.83		8.12	54.65
- K						15.26	3.76		8.05	54.60
- L						15.09	3.77		8.02	54.60
- M						15.08	3.79		8.10	54.55

Table 2.41 (contd.)

Complex	Calculated					Found				
	C%	H%	N%	Co%	X%[a]	C%	H%	N%	Co%	X%[a]
$[Co(pn)(dpt)Br]CdBr_4$ - L				7.59	51.47				7.63	51.30
- K									7.69	51.25
$[Co(pn)(dpt)NO_2]ZnCl_4$ - J	20.85	5.28		11.39	27.43	20.95	5.28		11.35	27.50
- L						21.02	5.46		11.33	27.55
- M						20.89	5.38		11.30	27.50
$[Co(pn)(dpt)NO_2]ZnCl_2.H_2O$ - K	20.26	5.40		11.05	26.58	20.38	5.68		11.18	26.75

[a] Total halide as found by Ag^+ titration

CH_3CO_2H at 40° (1 g/50 ml) and then adding 12 F HCl (30 ml/1 g) containing $ZnCl_2$ (2.5 g/1 g). The purified product that was deposited on cooling the solution to room temperature was collected in fractions and was washed and dried as above.

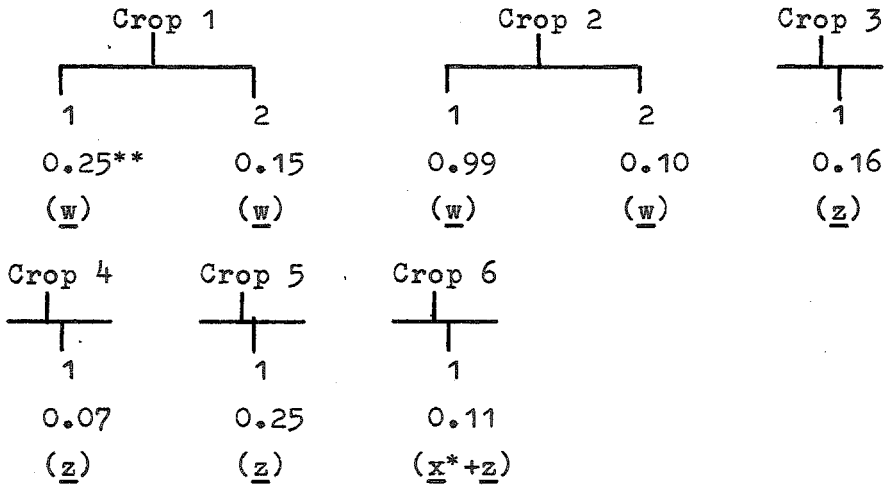
Further product was obtained on the slow evaporation of the aqueous mother liquor at room temperature (final volume 45 ml). These were recrystallised as above but using a corresponding reduction in the weights and volumes of the reagents used.

The total yield of chloropentaamine product was only 2.08 g or 3.9%. The isomeric composition of each fraction of recrystallised product is listed in Table 2.42.

Method B: trans-$Co(dpt)Cl_3$ (14 g) was suspended in water (20 ml) and isobutylenediamine (2.5 ml, 100%) was added. The solution was heated on a steam bath (ca. 80°) for 30 min. and then it was cooled in an ice bath. 12 F HCl (25 ml) containing $ZnCl_2$ (10 g) was added and the isobutylenediamine dihydrochloride that was immediately deposited was separated by filtration. The filtrate was allowed to stand at room temperature and after two days the purple product that slowly deposited was collected, washed with 2-propanol and then ether. The crude product was recrystallised by dissolving it in 0.2 F CH_3CO_2H at 35° (0.1 g/5 ml) and then adding 12 F HCl (5 ml/0.1 g) containing $ZnCl_2$ (0.5 g/0.1 g).

Table 2.42

Isomeric Compositions of $[Co(ibn)(dpt)Cl]ZnCl_4 \cdot xH_2O$; Method A



* denotes major component of fraction

** weight in g

The purified product, that was deposited on cooling the solution to room temperature, was collected in fractions and was washed and dried as above.

Further product was obtained on the slow evaporation of the aqueous mother liquor at room temperature (final volume 15 ml). These were recrystallised as above but using a corresponding reduction in the weights and volumes of the reagents used.

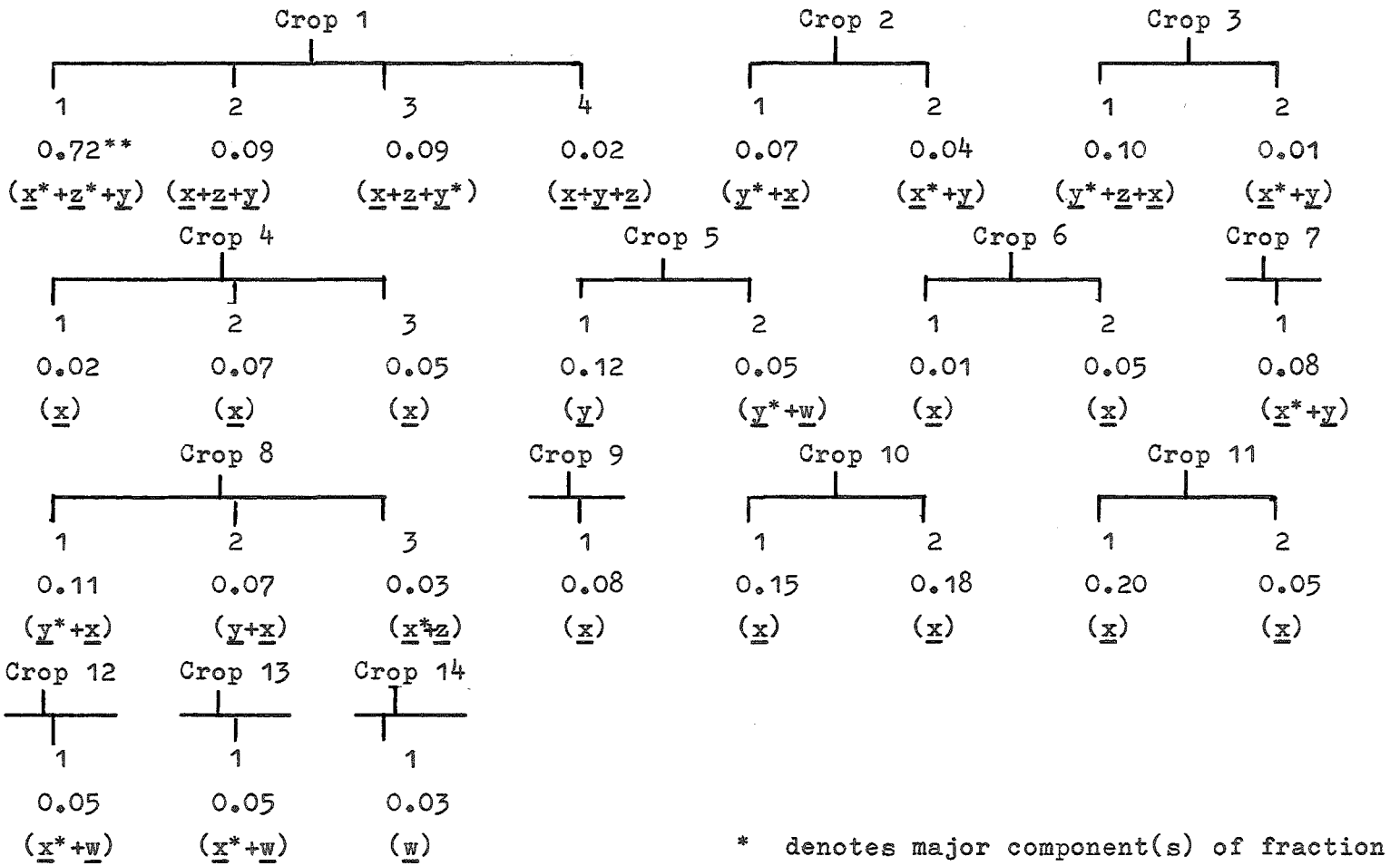
The total yield of chloropentaamine product was 2.59 g or 21.2%. The isomeric composition of each fraction of recrystallised product is listed in Table 2.43.

w and x-chloro(isobutylenediamine)(dipropylenetriamine) cobalt(III) Tetrabromocadmiumate(II): The w and x isomers of $[Co(ibn)(dpt)Cl]ZnCl_4$ were separately dissolved in 0.2 F CH_3CO_2H at 40° (0.25 g/15 ml) and a solution of 50% HBr (10ml) containing $CdBr_2.4H_2O$ (2.5 g) was added. The products that were immediately deposited, were collected from the ice cooled solutions, washed with 2-propanol and then ether. The yields were w 95.1%, x 92.3%.

Qualitative Isomerisation Reactions: Small quantities of the pure isomers were taken and subjected to the following chemical reactions. The isomeric composition of the chloro $ZnCl_4^{2-}$ salts was determined by examination of the infrared spectrum.

Table 2.43

Isomeric Compositions of $[Co(ibn)(dpt)Cl]ZnCl_4 \cdot xH_2O$; Method B



* denotes major component(s) of fraction

** weight in g

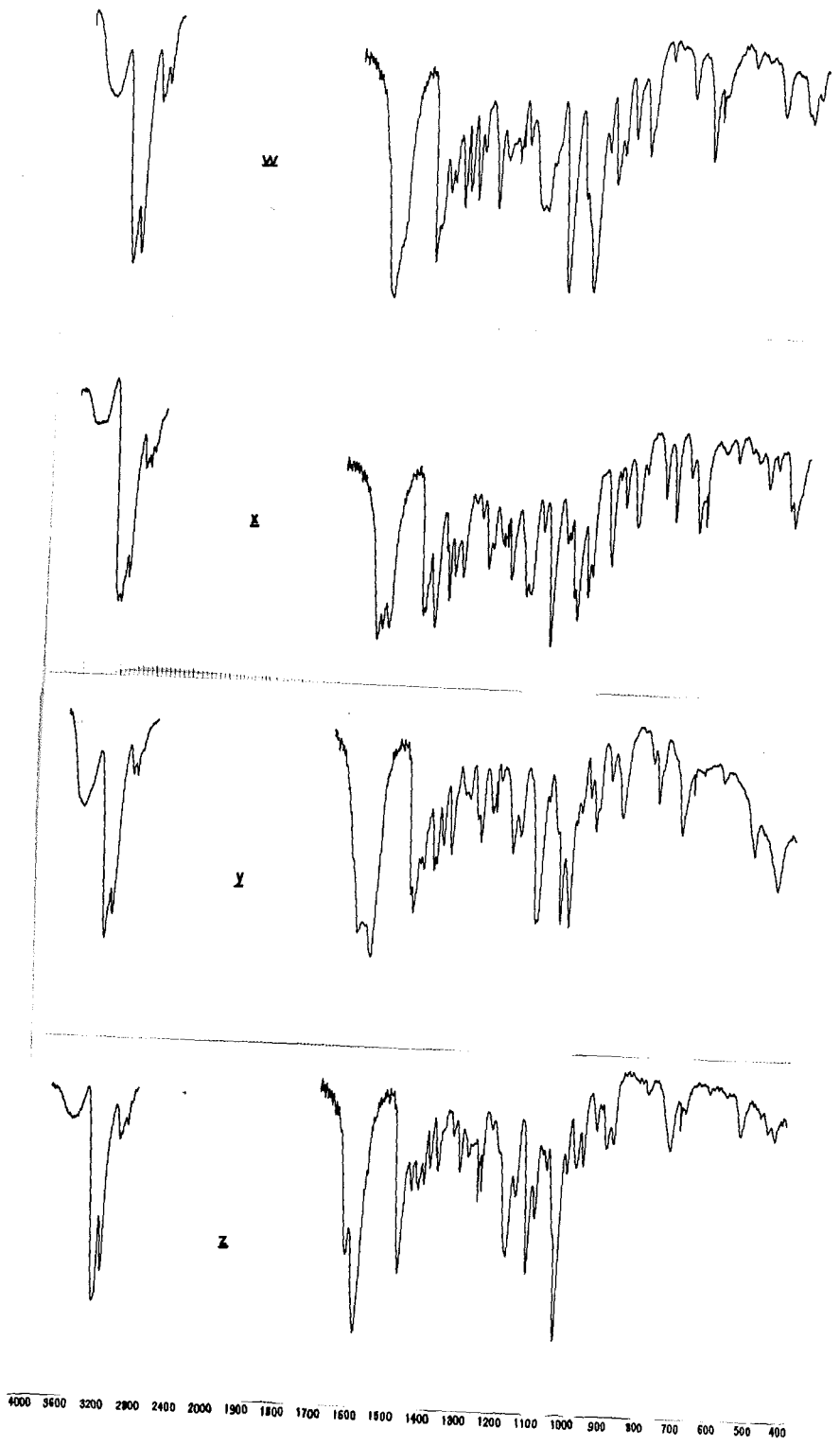


Figure 2.18 Infrared spectra of W, X, Y and Z - $[Co(ibn)(dpt)Cl]ZnCl_4 \cdot xH_2O$ in the range 4000-400 cm^{-1} (KBr Disc).

(a) Reaction with Nitrous Acid: The w, x, y and z isomers of $[Co(ibn)(dpt)Cl]ZnCl_4.xH_2O$ were separately dissolved in 0.1 F HCl (0.2 g/15 ml) and $NaNO_2$[13] was added. The solutions were heated on a steam bath (ca. 80°) for 10 min. during which time mild effervescence occurred and the colour changed from purple-red to orange. 12 F HCl (10 ml) was then added and the solutions were heated for a further two hours during which time the colour changed from orange to purple-red. $ZnCl_2$ (3 g) was then added and the products that deposited, were collected from the ice cooled solutions, washed with 2-propanol and then ether. The transformations that resulted were w → w+x; x → x; y → y; z → z+y.

(b) Base Hydrolysis: The w, x, y and z isomers of $[Co(ibn)(dpt)Cl]ZnCl_4.xH_2O$ were separately dissolved in water (0.1 g/5 ml) and 1 F NaOH (10 ml) was added. After standing the solutions at room temperature for 30 min., 12 F HCl (15 ml) containing $ZnCl_2$ (2.5 g) was added. The solutions were left to stand at room temperature and the product, that was deposited slowly, was collected, washed with 2-propanol and then ether. The results were w → w; x → w; y → z; z → z.

Table 2.44

Analytical Data for [Co(ibn)(dpt)Cl]X

Complex	Calculated				Found			
	C%	H%	Co%	X%[a]	C%	H%	Co%	X%[a]
$[Co(ibn)(dpt)Cl]ZnCl_4$ - w	23.06	5.61	11.31	34.03	23.10	5.66	11.37	33.75
- x					23.23	5.64	11.41	33.90
- z					23.03	5.62	11.25	33.87
$[Co(ibn)(dpt)Cl]ZnCl_4.H_2O$ - y	22.29	5.80	10.93	32.89	22.16	5.83	10.85	32.75
$[Co(ibn)(dpt)Cl]CdBr_4$ - w			7.90	47.61			7.82	47.42
- x							7.93	47.55

[a] Total halide as found by Ag^+ titration

(4) Stilbenediamine

Analytical data for the chloro isomers are presented in Table 2.46. Infrared spectra of the chloro $ZnCl_4^{2-}$ salts in the region 4000-400 cm^{-1} are presented in Fig. 2.19.

Isomers of Chloro(stilbenediamine)(dipropylenetriamine) cobalt(III) Tetrachlorozincate(II): trans-$Co(dpt)Cl_3$ (10 g) was suspended in methanol (100 ml) and stilbenediamine (8 g) was added. The solution was boiled under reflux for 15 min. during which time the green neutral complex dissolved to give a dark purple solution. 12 F HCl (25 ml) containing $ZnCl_2$ (10 g) was then added and after cooling the solution to room temperature the stilbenediamine dihydrochloride that deposited was removed by filtration. Methanol (30 ml) was then added to the filtrate and the crude product that deposited after six hours was collected in crops, washed with 2-propanol and then ether. The crude product was recrystallised by dissolving it in methanol (1 g/80 ml) at 60° and then adding 12 F HCl (10 ml/1 g) containing $ZnCl_2$ (2.5 g/1 g). The purified product that deposited on cooling, was collected in fractions and was washed and dried as above.

The mother liquor deposited further crops of crude product on slow evaporation at room temperature and these were recrystallised as above but using a corresponding reduction in the weights and volumes of the reagents used.

The total yield of chloropentaamine isomers was 13.27 g or 61.0%. The isomeric composition of each fraction of recrystallised product is listed in Table 2.45.

(F) Complexes of 1,3-diamines with dipropylenetriamine

(1) 1,3-propanediamine

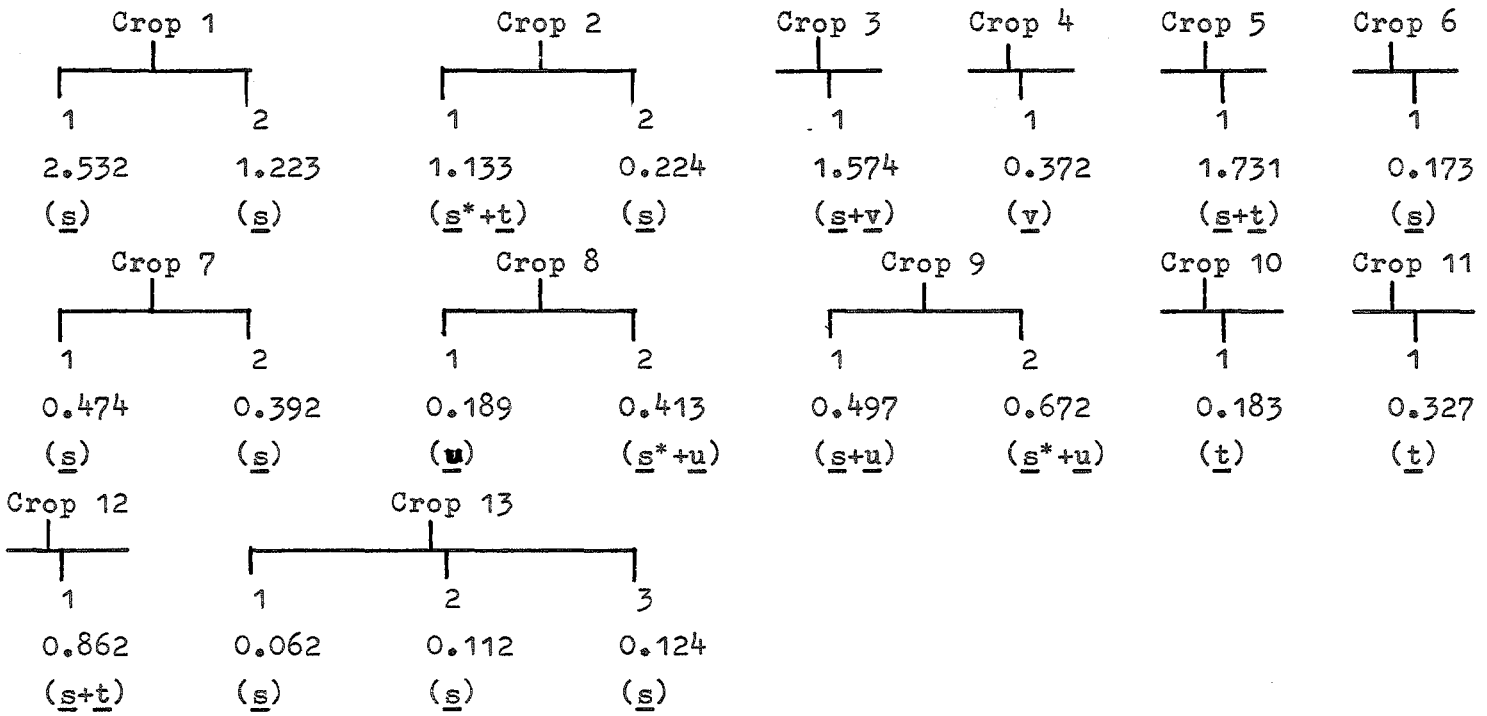
Analytical data for the complexes are presented in Table 2.50. Infrared spectra of the chloro $ZnCl_4^{2-}$ salts in the region 4000-400 cm^{-1} are presented in Fig. 2.20 and 2.21.

μ-Peroxobis(1,3-propanediamine)bis(dipropylenetriamine) dicobalt(III) Perchlorate Trihydrate: An aqueous solution of 1,3-propanediamine (7.4 g) and dipropylenetriamine (13.1 g) in water (200 ml) was added to a stirred solution of $Co(NO_3)_2.6H_2O$ (29 g) and $NaClO_4.H_2O$ (50 g) in 500 ml of water. A rapid stream of O_2 gas was passed through the stirred, room temperature solution and after two hours the brown crystals that deposited were collected, washed with 2-propanol, and then ether and finally air dried. The yield was 37 g or 74%.

A sample for analysis was prepared by dissolving 2 g of the crude product in the minimum volume (ca. 80 ml) of room temperature water. After filtration, excess

Table 2.45

Isomeric Compositions of fractions of $[Co(stien)(dpt)Cl]ZnCl_4$



* denotes major component of fraction

** weight in g

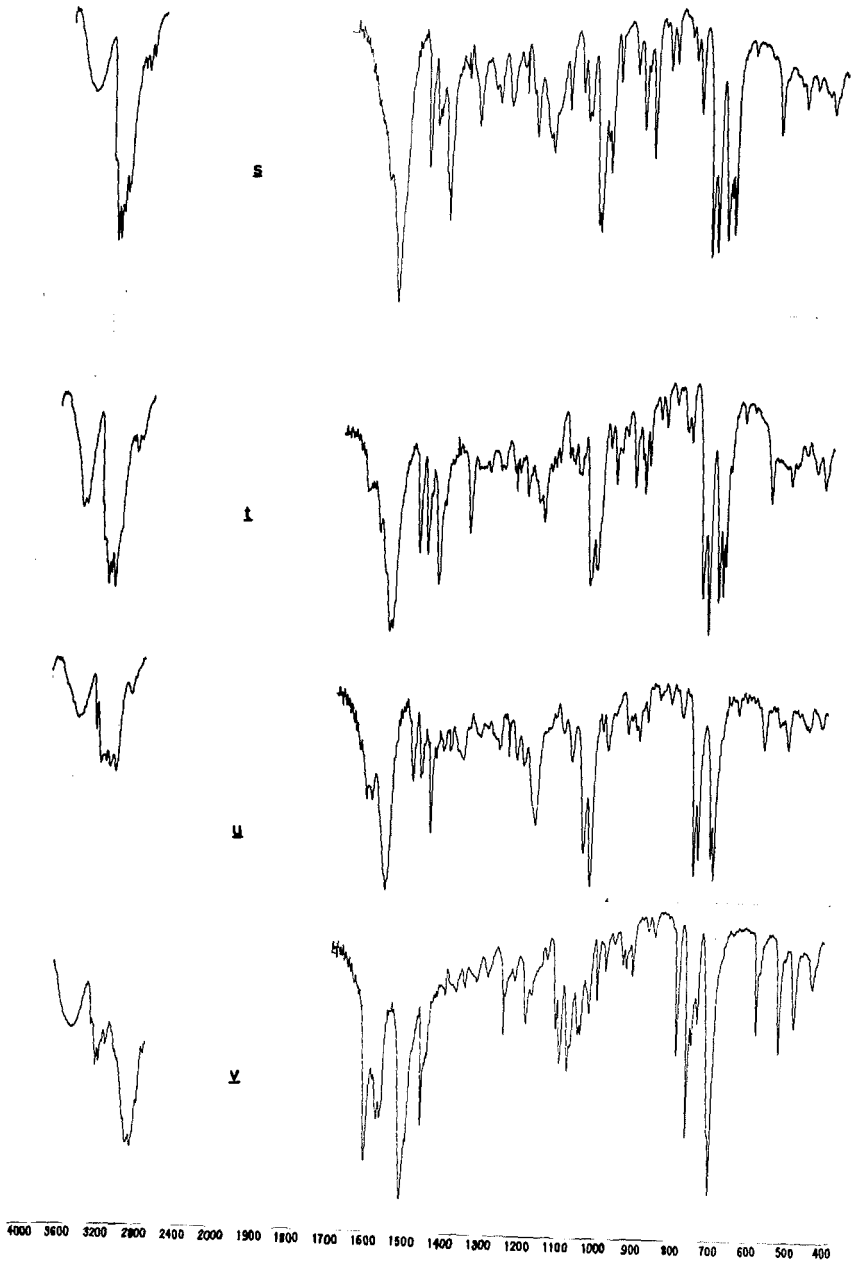
Table 2.46

Analytical Data for $[Co(stien)(dpt)Cl]ZnCl_4$

Complex	Calculated				Found			
	C%	H%	Co%	X%[a]	C%	H%	Co%	X%[a]
$[Co(stien)(dpt)Cl]ZnCl_4$ - s	37.24	5.16	9.14	27.48	37.01	5.11	9.03	27.32
- t					36.95	5.22	9.06	27.21
- u					36.94	5.14	9.22	27.44
- v					37.04	5.22	9.08	27.38

[a] Total halide as found by Ag^+ titration

Figure 2.19 Infrared spectra of s, t, u and v - [Co(stien)(dpt)Cl]$ZnCl_4$ in the region 4000-400 cm^{-1} (KBr Disc).



$NaClO_4.H_2O$ was added to the stirred solution and the brown crystalline product that deposited was collected, washed and dried as above. A 60% recovery was obtained.

Isomers of Chloro(1,3-propanediamine)(dipropylenetriamine) cobalt(III) Tetrachlorozincate(II):

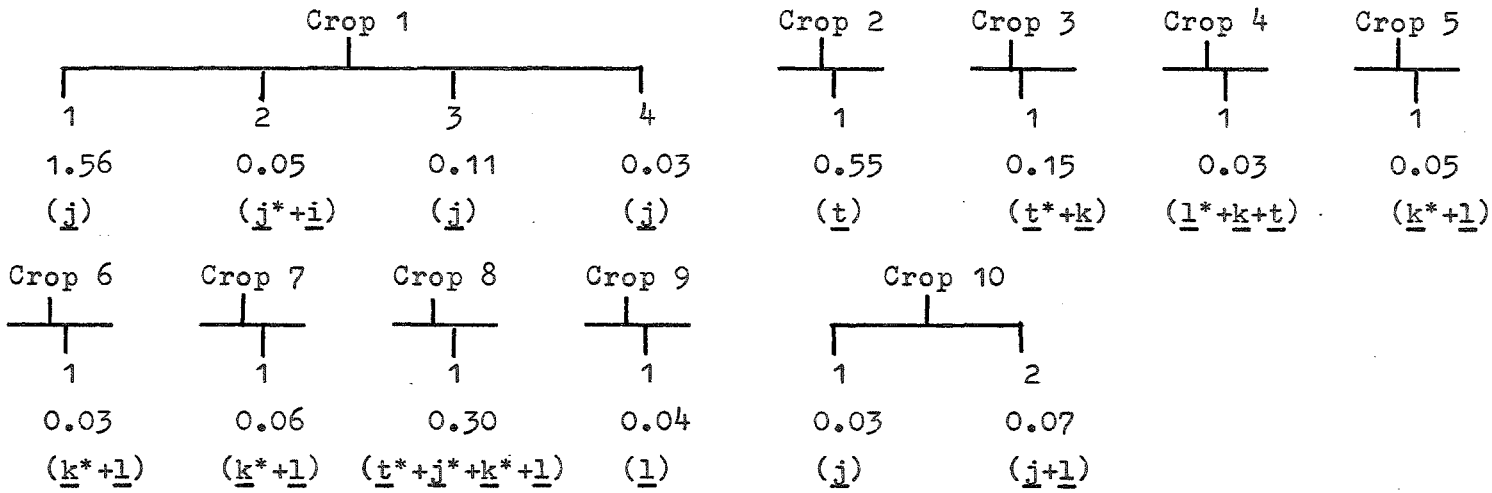
Method A: trans-$Co(dpt)Cl_3$ (5 g) was suspended in water (25 ml) and 1,3-propanediamine (2.5 ml, 100%) was added. The purple-red solution was heated at 60° for 10 mins and then 12 F HCl (15 ml) was added dropwise. $ZnCl_2$ (5 g) dissolved in water (10 ml) was then added and on cooling to room temperature the crude product slowly deposited. This material was recrystallised by dissolving it in 0.2 F HCl at 60° (1 g/40 ml) and then adding 12 F HCl (10 ml/1 g) and $ZnCl_2$ (2.5 g/1 g). The crystalline product that deposited on cooling was collected in fractions and was washed and dried as above.

The aqueous mother liquor was reheated to 80° to evaporate it to ca. 40 ml. Further crops were obtained on standing at room temperature, the first of these containing a large percentage of trans-$[Co(tmd)_2Cl_2]Cl$. The crops were recrystallised as above but using a corresponding reduction in volumes and weights of the reagents used.

The total yield of chloropentaamine product was 2.21 g or 26.2%. The isomeric composition of the fractions are listed in Table 2.47.

Table 2.47

Isomeric Composition of $[Co(tmd)(dpt)Cl]ZnCl_4$; Method A



* denotes the major component(s) of the fraction

** weight in g

t trans - $[Co(tmd)_2Cl_2]Cl$

Method B: Crude $[Co_2(tmd)_2(dpt)_2O_2](ClO_4)_4.3H_2O$ (35 g) was added to a solution of 12 F HCl (100 ml) in water (200 ml) containing $ZnCl_2$ (60 g). The solution was heated on a steam bath (ca. 80°) until the effervescence ceased (2.5 hr) during which time a red crystalline material deposited.

The solution was cooled to 5° in an ice bath and the crude product was then collected, washed with 2-propanol and then ether.

The crude product was recrystallised by dissolving it in 0.2 F HCl at 80° (1 g/25 ml) and then adding 12 F HCl (5 ml/1 g) and $ZnCl_2$ (2.5 g/1 g). The purified product that deposited on cooling was collected in fractions and was washed and dried as above.

On further evaporation of the aqueous mother liquor, further crops were obtained and these were recrystallised as above but using a corresponding reduction in the volumes and weights of the reagents used.

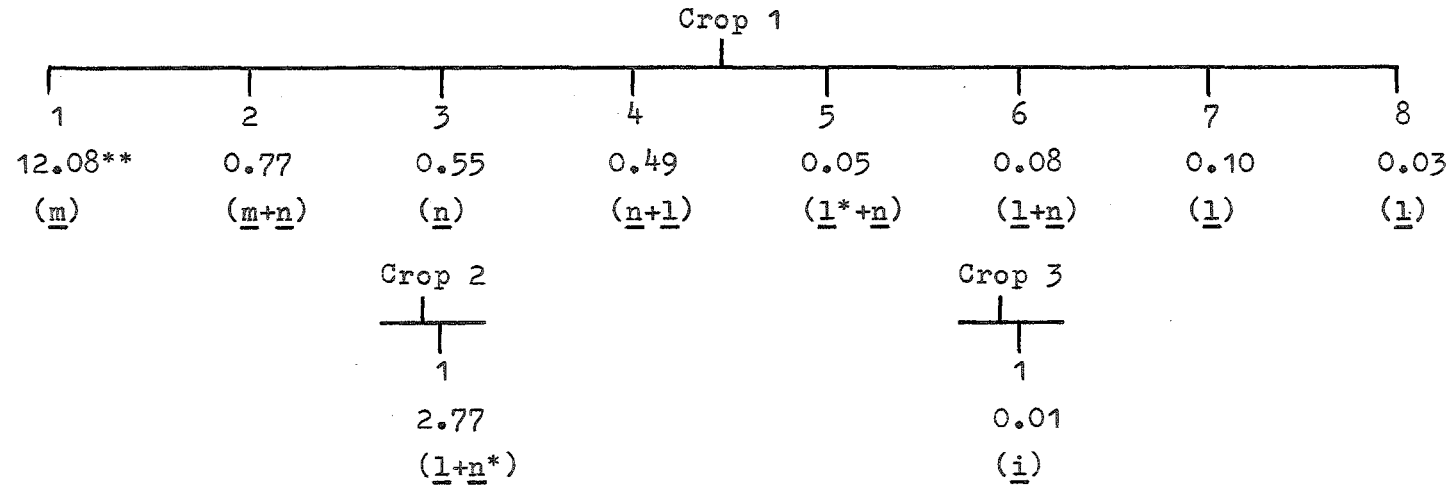
The total yield of chloropentamine product was 16.93 g or 50.9%. The isomeric compositions of the fractions are listed in Table 2.48.

Qualitative Isomerisation Reactions - $[Co(tmd)(dpt)Cl]ZnCl_4$

(a) Reflux in 6 F HCl: The pure i and j isomers of $[Co(tmd)(dpt)Cl]ZnCl_4$ were separately dissolved in 6 F HCl (0.5 g/25 ml) and the solutions were boiled under reflux for 30 min. 12 F HCl (5 ml) containing $ZnCl_2$ (5 g) was

Table 2.48

Isomeric Compositions of $[Co(tmd)(dpt)Cl]ZnCl_4$; Method B



* indicates the major component(s) of the fraction

** weight in g

added and the products that were slowly deposited from the ice cooled solutions were collected in crops and washed with 2-propanol and then ether.

The results were: i → i*+l*+j+k; j → i*+l*+j+k. (* denotes the major components of the product.)

(b) Base Hydrolysis (20-23°): The pure isomers of $[Co(tmd)(dpt)Cl]ZnCl_4$ were separately dissolved in water (0.25 g/8 ml) and ca. 10 ml of 1 F NaOH was added until all the $Zn(OH)_2$ had precipitated. The red solutions were allowed to stand at room temperature for 20 min. and then 12 F HCl (10 ml) and $ZnCl_2$ 2.5 g) were added. On standing the solutions at room temperature for one day, the product was slowly deposited and it was collected in crops, washed with 2-propanol and then ether.

The results were: i → i; j → i; k → i; l → i.

(c) Reaction with Nitrous Acid: Nitro compounds derived from the pure isomers of $[Co(tmd)(dpt)Cl]ZnCl_4$ were prepared using the method described later. The nitro products were decomposed by heating (80°) a solution of each in 3 F HCl for one hour. The $ZnCl_4^{2-}$ salts of the chloro complexes were deposited by the addition of $ZnCl_2$.

The transformations that resulted were: i → i; j → i; k → i; l → i.

The infrared spectra of the nitro products indicate that these form with the same gross configuration as the

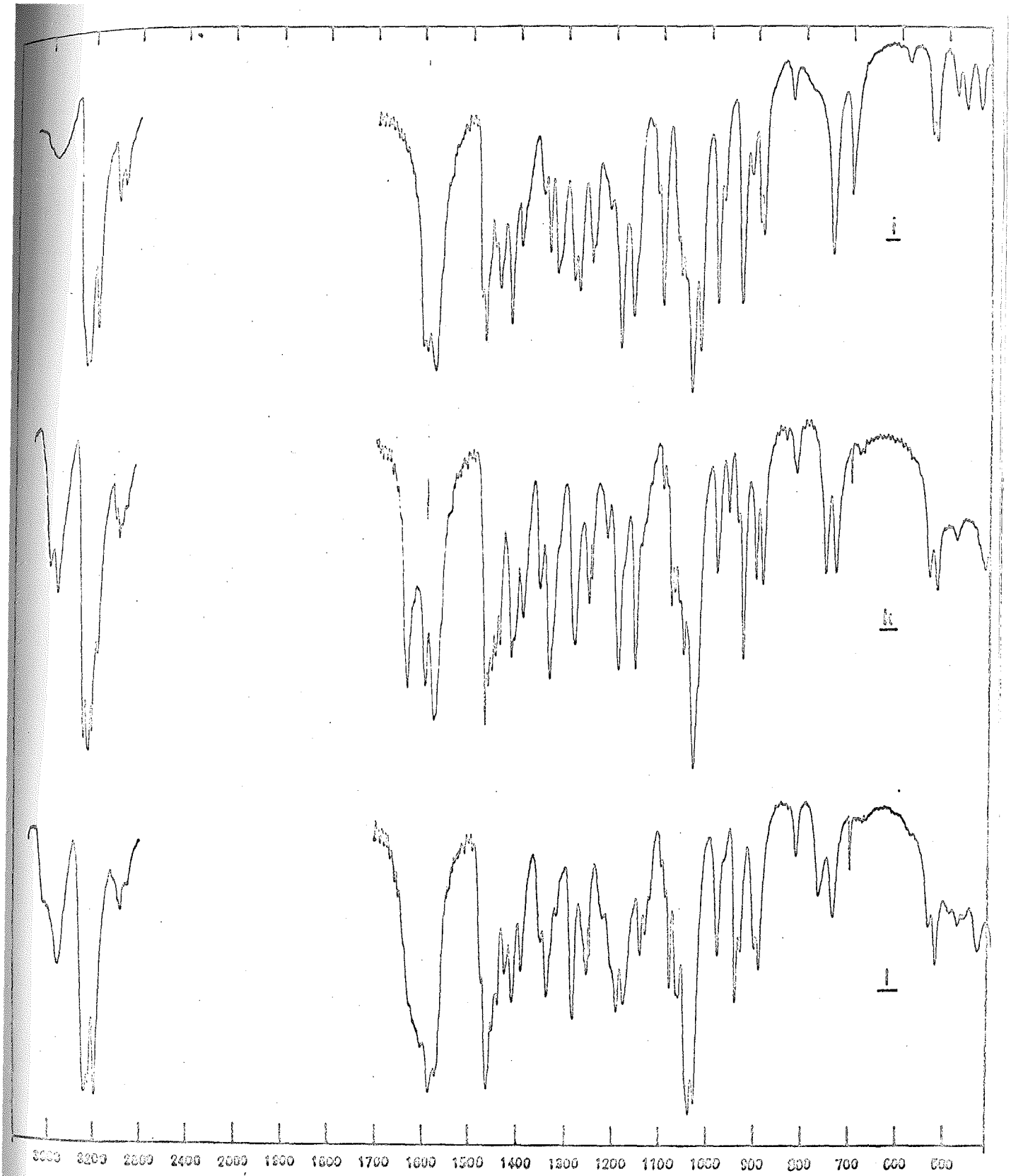


Figure 2.20 Infrared spectra of i, k and l - $[Co(tmd)(dpt)Cl]ZnCl_4.xH_2O$ in the range 4000-400 cm^{-1} (KBr Disc).

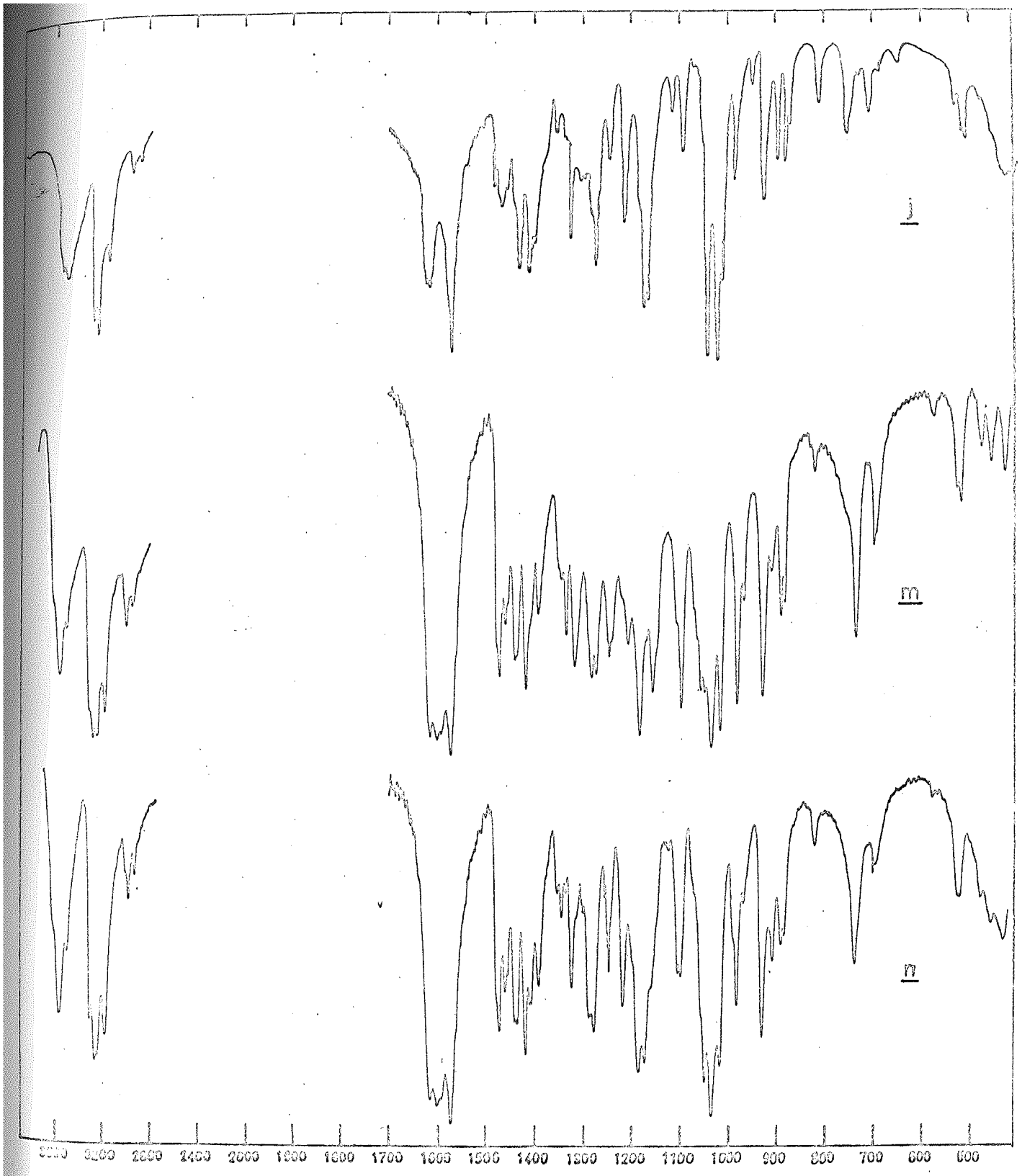


Figure 2.21 Infrared spectra of j, m and n - $[Co(tmd)(dpt)Cl]ZnCl_4.xH_2O$ in the range 4000-400 cm^{-1} (KBr Disc).

parent chloro isomer, i.e. i,j → i; k,l → l. It is therefore probable that the isomerisation l → i occurs in the decomposition procedure above.

i-Chloro(1,3-propanediamine)(dipropylenetriamine)cobalt(III) Tetrachlorocadmiumate(II): i-$[Co(tmd)(dpt)Cl]ZnCl_4$ (0.5 g) was dissolved in 0.2 F CH_3CO_2H (15 ml) at 50° and a solution of 4 F HCl (25 ml) containing $CdCl_2$ (5 g) was added. The mauve-red product deposited slowly on cooling in an ice bath and it was collected, washed with 2-propanol and ether. The yield was 87.1%.

i,j and l-Chloro(1,3-propanediamine)(dipropylenetriamine) cobalt(III) Tetrabromozincate(II): The i, j and l isomers of $[Co(tmd)(dpt)Cl]ZnCl_4.xH_2O$ were separately dissolved in 0.2 F CH_3CO_2H (1 g/80 ml, 0.25 g/25 ml, 0.25 g/25 ml respectively) at 50° and a solution of 63% HBr (25 ml, 15 ml, 25 ml) containing $ZnBr_2$ (5 g, 2.5 g, 2 g) was added. The mauve, mauve-red and violet products that were deposited slowly on cooling to room temperature were collected from the ice cooled solutions and were washed with 2-propanol and then ether. The yields were: i, 95.0%; j, 77.8% and l, 65.0%.

i and j-Chloro(1,3-propanediamine)(dipropylenetriamine) cobalt(III) Tetrabromocadmiumate(II): The i and j isomers of $[Co(tmd)(dpt)Cl]ZnCl_4.xH_2O$ were separately dissolved in 0.2 F CH_3CO_2H (0.25 g/15 ml) and a solution of 63% HBr (10 ml) containing $CdBr_2.4H_2O$ (2.5 g) was added. On cooling to room temperature, the mauve and purple-red products were deposited and they were collected from the ice cooled solutions, washed with 2-propanol and then ether. The yields were: i 74.3%, j 82.1%.

i, j and l-Chloro(1,3-propanediamine)(dipropylenetriamine) cobalt(III) Perchlorate: The i, j and l isomers of $[Co(tmd)(dpt)Cl]ZnCl_4.xH_2O$ were separately dissolved in 0.2 F CH_3CO_2H (0.5 g/25 ml, 0.3 g/15 ml, 0.5 g/25 ml respectively) at 40° and $NaClO_4.H_2O$ (15 g, 10 g, 5 g) was added. The mauve, mauve and violet perchlorate salts were deposited on cooling in an ice bath and they were collected, washed with 2-propanol and then ether. The yields were: i, 82.9%, j, 81.1% and l, 40.6%.

i, j and l-Chloro(1,3-propanediamine)(dipropylenetriamine) cobalt(III) Tetrathiocyanatozincate(II): The i, j and l isomers of $[Co(tmd)(dpt)Cl]ZnCl_4.xH_2O$ were separately dissolved in 0.2 F CH_3CO_2H (1 g/150 ml, 0.25 g/40 ml, 0.25 g/15 ml respectively) at 50° and a solution of NH_4SCN (3 g, 2.5 g, 2 g) in water (20 ml, 10 ml, 5 ml) was

added. The mauve, mauve and violet tetrathiocyanatozincate (II) salts were deposited slowly on cooling in an ice bath and they were collected, washed with 2-propanol and then ether. The yields were: i, 72.7%; j, 96.2%; l, 76.0%.

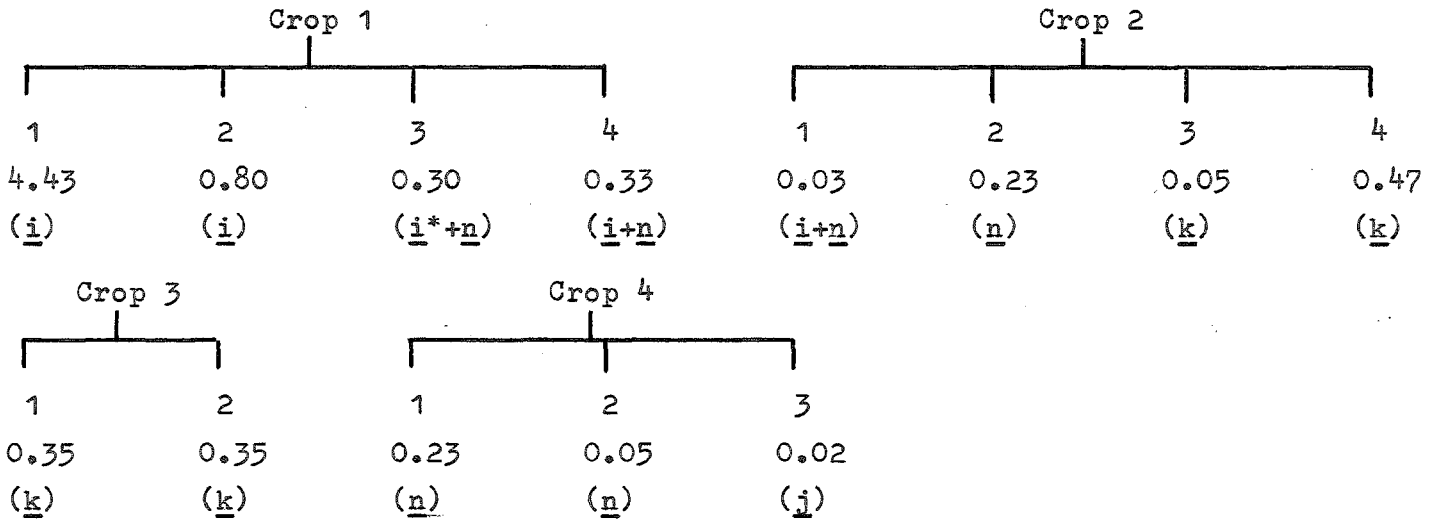
Isomers of Bromo(1,3-propanediamine)(dipropylenetriamine) cobalt(III) Tetrabromozincate(II)

Method A: $[Co_2(tmd)_2(dpt)_2O_2](ClO_4)_4.3H_2O$ (16 g) was added to a solution of 50 ml 63% HBr in 100 ml of water. The solution was heated on a steam bath (ca. 80°) for 30 min. during which time there was mild effervescence and some bromine was evolved. $ZnBr_2$ (20 g) was then added and the solution was reheated for a further 30 min. The crude product was recrystallised by dissolving it in 0.2 F CH_3CO_2H (1 g/25 ml) at 80°, filtering to remove the di-tribromide salt (see below), and then adding 63% HBr (5 ml/1 g) and $ZnBr_2$ (2.5 g/1 g). The purified product that deposited was collected in fractions, washed and dried as above.

Further crops were obtained from the aqueous mother liquor on cooling in an ice bath and these were recrystallised as above but using a corresponding reduction in the weights and volumes of the reagents used. The yield was 33.0% (3.8% as the tribromide salt). The isomeric compositions of the fractions are listed in Table 2.49.

Table 2.49

Isomeric Composition of $[Co(tmd)(dpt)Br]ZnBr_4$



* denotes the major component(s) of the fraction

** weight in g

Method B: A solution of i-[Co(tmd)(dpt)Cl]$ZnCl_4$ (0.5 g) in water (10 ml) containing 63% HBr (2 ml) was boiled under reflux for 20 min. The hot solution was added to a solution of $ZnBr_2$ (2.5 g) in 63% HBr (5 ml) and the product that deposited on cooling to room temperature, was collected in crops, washed with 2-propanol and then ether. The yield was 73.5%. The isomeric composition of the product was, in the order: crop number, isomer composition (* indicates the major isomeric component), (weight in g): 1, j, (0.18); 2, k*+j, (0.11); 3 → 6, k, (0.24).

Method C: An analogous reaction to the above using j-[Co(tmd)(dpt)Cl]$ZnCl_4.2H_2O$. A 67.6% yield was obtained and the isomeric composition of the product was: 1, j*+k, (0.18); 2, k*+j, (0.20); 3, k*+j, (0.03); 4 → 6, k, (0.13).

i-Bromo(1,3-propanediamine)(dipropylenetriamine)cobalt(III) Di-tribromide: $[Co_2(tmd)_2(dpt)_2O_2](ClO_4)_4.3H_2O$ (8 g) was added to 63% HBr (25 ml) in water (50 ml). The solution was heated on a steam bath (ca. 80°) for 10 min. during which time mild effervescence occurred and a brown crystalline substance was deposited. The product was collected, washed with 2-propanol and then ether. The yield was 14.6%.

Further heating of the mother liquor and the addition of $ZnBr_2$ (5 g) resulted in the deposition of the i and n isomers as in the previous synthesis, Method A.

i-Bromo(1,3-propanediamine)(dipropylenetriamine)cobalt(III) Di-bromide: $[Co_2(tmd)_2(dpt)_2O_2](ClO_4)_4 \cdot 3H_2O$ (2 g) was suspended in water (10 ml) and 63% HBr (30 ml) was added. The solution was heated on a steam bath (ca. 80°) for 15 min. during which time a purple-violet product was deposited. This product was collected from the ice cooled solution, washed with 2-propanol and then ether. The yield was 17.0%.

i-Bromo(1,3-propanediamine)(dipropylenetriamine)cobalt(III) Tetrachlorozincate(II): i-$[Co(tmd)(dpt)Br]ZnBr_4$ (0.5 g) was dissolved in 0.05 F HBr (45 ml) at 60° and a solution of 12 F HCl (25 ml) containing $ZnCl_2$ (2 g) was added. The violet-purple product deposited immediately and, after cooling the solution in an ice bath, it was collected, washed with 2-propanol and ether. The yield was 96.3%.

i-Bromo(1,3-propanediamine)(dipropylenetriamine)cobalt(III) Tetrathiocyanatozincate(II): i-$[Co(tmd)(dpt)Br]ZnCl_4$ (0.25 g) was dissolved in 0.2 F CH_3CO_2H (10 ml) and a solution of NH_4NCS (2.5 g) in water (10 ml) was added. The pale purple product deposited immediately and it was collected, washed with 95% ethanol and then air-dried. The yield was 85.0%.

i-Bromo(1,3-diaminopropane)(dipropylenetriamine)cobalt(III) Perchlorate: i-[Co(tmd)(dpt)Br]$ZnBr_4$ (0.5 g) was dissolved in 3 F $HClO_4$ (25 ml) at 80° and $NaClO_4.H_2O$ (5 g) was added. The violet-purple crystalline product deposited on cooling the solution in an ice bath. The product was collected, washed with 2-propanol and then ether. The yield was 85.2%.

i and k-Bromo(1,3-diaminopropane)(dipropylenetriamine) cobalt(III) Tetrabromocadmiumate(II): The i and k isomers of [Co(tmd)(dpt)Br]$ZnBr_4$ (0.5 g, 0.25 g, respectively) were separately dissolved in 0.2 F CH_3CO_2H (10 ml, 15 ml) at 50° and a solution of 63% HBr (15 ml, 10 ml) containing $CdBr_2.4H_2O$ (5 g, 2.5 g) was added. The purple products were deposited on cooling and they were collected from the ice cooled solutions, washed with 2-propanol and then ether. The yields were: i, 84.3%, k 63.2%.

i-Hydroxo(1,3-propanediamine)(dipropylenetriamine)cobalt (III) Perchlorate: i-[Co(tmd)(dpt)Cl]$ZnCl_4$ (2 g) and Ag_2O (2.4 g) were suspended in water (50 ml). The mixture was warmed at 60° for 30 min. and then it was filtered. $NaClO_4.H_2O$ (5 g) was added to the violet filtrate which was then evaporated to ca. 10 ml at 25° under a slow stream of air. After four days, pale violet needle-like crystals were deposited and these were collected, washed with methanol and air dried. The yield was 35%.

i-Azido(1,3-propanediamine)(dipropylenetriamine)cobalt(III) Tetrachlorozincate(II): *i*-$[Co(tmd)(dpt)Cl]ZnCl_4$ (2 g) was dissolved in 0.2 *F* CH_3CO_2H (40 ml) and NaN_3 (6 g) was added. The solution was heated on a steam bath (*ca*. 80°) for 15 min., cooled to *ca*. 25° in an ice bath and 1:1 2-propanol/methanol (100 ml) containing $ZnCl_2$ (5 g) and 12 *F* HCl (1 ml). On standing at 0-5° for 24 hours the product, that slowly deposited, was collected, washed with 2-propanol and then ether. The yield was 61.2%.

i-Azido(1,3-propanediamine)(dipropylenetriamine)cobalt(III) Tetrabromozincate(II): *i*-$[Co(tmd)(dpt)N_3]ZnCl_4$ (0.25 g) was dissolved in 0.05 *F* HCl (20 ml) and a solution of 63% HBr (20 ml) containing $ZnBr_2$ (2 g) was added. The red-purple crystalline product deposited on cooling the solution in an ice bath. The product was collected, washed with 2-propanol and then ether. The yield was 87.3%.

i-Azido(1,3-propanediamine)(dipropylenetriamine)cobalt(III) Tetrathiocyanatozincate(II): *i*-$[Co(tmd)(dpt)N_3]ZnCl_4$ (0.25 g) was dissolved in 0.2 *F* CH_3CO_2H (25 ml) and a solution of NH_4NCS (2 g) in water (5 ml) was added. The red-purple product which deposited on cooling the solution in an ice bath was collected, washed with 95% ethanol and air dried. The yield was 73.2%.

i and l-Nitro(1,3-propanediamine)(dipropylenetriamine) cobalt(III) Tetrachlorozincate(II): The i and l isomers of $[Co(tmd)(dpt)Cl]ZnCl_4.xH_2O$ were separately dissolved in 0.2 F HCl (2 g/50 ml, 0.25 g/10 ml, respectively) and $NaNO_2$ (6 g, 1 g) was added. The solutions were heated on a steam bath (ca. 80°) for 30 min. during which time mild effervescence occurred and the colour changed rapidly from red to yellow-orange. The hot solutions were slowly poured into 1:1 2-propanol/acetone (200 ml, 50 ml) containing $ZnCl_2$ (5 g, 2.5 g) and 12 F HCl (1 ml, 0.5 ml). The orange-yellow products were deposited on cooling to room temperature and they were collected from the ice cooled solutions, washed with acetone and then ether. The yields were: i, 90.3%, l, 73.8%.

i-Nitro(1,3-propanediamine)(dipropylenetriamine)cobalt(III) Perchlorate: i-$[Co(tmd)(dpt)Cl]ZnCl_4$ (2 g) was dissolved in 0.2 F HCl (50 ml) and $NaNO_2$ (6 g) was added. The solution was heated on a steam bath (ca. 80°) for 30 min. Mild effervescence occurred and the colour changed from red to orange-yellow. $NaClO_4.H_2O$ (5 g) was added to the hot solution which was slowly poured into 1:1 2-propanol/acetone containing $NaClO_4.H_2O$ (5 g) and 4 F $HClO_4$ (1 ml). On standing at room temperature for three days, the orange crystals that were slowly deposited were collected, washed with 2-propanol and then ether. The yield was 80%.

Table 2.50

Analytical Data for [Co(tmd)(dpt)X]Y

Complex	Calculated					Found				
	C%	H%	N%	Co%	X%*	C%	H%	N%	Co%	X%*
$[Co_2(tmd)_2(dpt)_2O_2](ClO_4)_4.3H_2O$	21.35	5.96	13.84	11.65	-	21.25	5.76	13.79	11.73	-
$[Co(tmd)(dpt)Cl]ZnCl_4.2H_2O$ - j	19.90	5.75	12.87	10.84	32.62	19.64	5.55	12.84	10.88	32.81
- m						19.81	5.61	12.82	10.75	32.75
$[Co(tmd)(dpt)Cl]ZnCl_4.H_2O$ - n	20.60	5.56	13.35	11.23	33.81	20.74	5.70	13.24	11.29	33.65
- l						20.89	5.58	13.23	11.12	33.92
- k						20.55	5.60	13.41	11.12	33.93
$[Co(tmd)(dpt)Cl]ZnCl_4$ - i	21.42	5.37	13.84	11.64	35.01	21.36	5.37	13.80	11.71	35.10
$[Co(tmd)(dpt)Cl]CdCl_4$ - i				10.64	32.00				10.71	31.92
$[Co(tmd)(dpt)Cl]ZnBr_4$ - i				8.61	51.86				8.52	51.41
- j									8.55	51.56
- l									8.49	51.60
$[Co(tmd)(dpt)Cl]CdBr_4$ - i				8.05	48.52				8.12	48.60
- j									8.00	48.55

Table 2.50 (contd.)

Complex	Calculated					Found				
	C%	H%	N%	Co%	X%*	C%	H%	N%	Co%	X%*
$[Co(tmd)(dpt)Cl](ClO_4)_2$ - i	21.68	5.44	14.05	11.82	7.11	21.59	5.60	13.83	11.71	7.05
- j						21.85	5.58	13.82	11.67	7.08
- l						20.99	5.46	13.30	11.45	6.91
$[Co(tmd)(dpt)Cl]Zn(SCN)_4$ - i	26.18	4.56	21.27	9.87	44.98	26.49	5.00	21.76	9.94	44.58
- j									9.85	44.95
- l									9.93	44.60
$[Co(tmd)(dpt)Br]ZnBr_4$ - i	14.82	3.73	9.61	8.08	54.79	15.05	3.85	9.35	7.91	54.61
- j						14.71	3.92		7.95	54.47
- n						14.74	3.79		7.90	54.50
$[Co(tmd)(dpt)Br]ZnBr_4.H_2O$ - k	14.47	3.91		7.89	53.47	14.57	4.00		7.82	53.69
$[Co(tmd)(dpt)Br](Br_3)_2$ - i	13.12	3.30		7.16	67.91	13.65	4.01		7.25	66.50
$[Co(tmd)(dpt)Br]Br_2$ - i				11.69	47.57				11.57	47.39
$[Co(tmd)(dpt)Br]ZnCl_4$ - i				10.69	40.21				10.41	40.27
$[Co(tmd)(dpt)Br]Zn(SCN)_4$ - i				9.18	48.64				9.08	48.29

Table 2.50 (contd.)

Complex	Calculated					Found				
	C%	H%	N%	Co%	X%*	C%	H%	N%	Co%	X%*
$[Co(tmd)(dpt)Br](ClO_4)_2$ - i				10.85	14.71				10.77	14.61
$[Co(tmd)(dpt)Br]CdBr_4$ - i				7.59	51.47				7.62	51.55
$[Co(tmd)(dpt)Br]CdBr_4.H_2O$ - k				7.42	50.30				7.45	50.55
$[Co(tmd)(dpt)OH](ClO_4)_2$ - i	22.51	5.88		12.27		22.01	5.65		12.06	
$[Co(tmd)(dpt)N_3]ZnCl_4$ - i	21.13	5.28	21.81	11.46	27.61	21.22	5.30	21.95	11.41	27.72
$[Co(tmd)(dpt)N_3]ZnBr_4$ - i	15.64	3.94	16.21	8.52	46.24	15.97	3.94	15.95	8.41	45.93
$[Co(tmd)(dpt)N_3]Zn(SCN)_4$ - i				9.76	38.45				9.71	38.18
$[Co(tmd)(dpt)NO_2]ZnCl_4$ - i	20.85	5.28	16.23	11.39	27.43	21.03	5.47	16.11	11.45	27.14
- l						20.89	5.11		11.40	27.53
$[Co(tmd)(dpt)NO_2](ClO_4)_2$ - i	21.23	5.35		11.57		20.78	5.25		11.53	
$[Co(tmd)(dpt)NO_2]Zn(SCN)_4$ - i				9.69	38.20				9.51	38.46

* Total halogen or NCS^- as found by Ag^+ titration

i-Nitro(1,3-propanediamine)(dipropylenetriamine)cobalt(III) Tetrathiocyanatozincate(II): i-$[Co(tmd)(dien)NO_2]ZnCl_4$ (1 g) was dissolved in 0.2 F CH_3CO_2H (60 ml) at 60° and a solution of NH_4NCS (10 g) dissolved in water (15 ml) was added. The orange-yellow product that deposited on cooling to room temperature was collected from the ice cooled solution, washed with 2-propanol and was then air dried. The yield was 95.8%.

(G) Spectral Measurements

The visible absorption spectra were obtained with a Cary 14 recording spectrophotometer and a Shimadzu MPS-50L recording spectrophotometer using matched 1 cm and 10 cm quartz cells. The visible reflectance spectra (Chapter 1) were obtained with the latter instrument. Spectrophotometric analyses for Co and Cr were performed using a Beckman DBG recording spectrophotometer. The optical rotatory dispersion spectra were obtained with a JASCO-ORD-UV5 recording spectropolarimeter using 1 cm, 5 cm and 10 cm quartz cells. The infrared spectra were measured in both nujol mulls and KBr discs using a Shimadzu IR-27G infrared spectrophotometer and a Perkin-Elmer 337 infrared spectrophotometer. Room temperature NMR spectra were measured in d_6-DMSO with external TMS standard using a Varian A-60 Analytical NMR Spectrometer.

(H) Chemical Analyses

Co was determined by decomposing the complexes with ammonium peroxodisulphate and estimating the Co(II) spectrophotometrically at 620 nm as the tetrathiocyanate complex in aqueoue acetone. Cr was analysed as CrO_4^{2-} by measuring the absorption spectrophotometrically at 372 nm after decomposition of the complex with hot alkaline ammonium peroxodisulphate. Halogen and thiocyanate were determined by potentiometric titration with standard $AgNO_3$ using a Radiometer pH meter. The complexes were base hydrolysed with sodium hydroxide for 10 min. and then acidified with HNO_3 prior to titration. C, H and N analyses were performed by Dr A.D. Campbell of the University of Otago, Dunedin, New Zealand.

C H A P T E R 3

OCTAHEDRAL COMPLEXES OF THE CHLOROPENTAAMINECOBALT(III) TYPE

RESULTS

RESULTS

A variety of new [Co(AA)(ABA)X]Z complexes have been synthesised and characterised. In any particular system, the greatest number of isomers isolated occurs when X = Cl^-. The infrared spectra of the chloro $ZnCl_4^{2-}$ salts (4000-400 cm^{-1} or 1700-400 cm^{-1} range) (KBr Discs) have already been presented in Chapter 2.

(1) Visible Absorption Spectra

Molar absorbancy index versus wavelength plots for all of the isomeric $M(AA)(ABA)Cl^{n+}$ complexes (M = Co,Cr) isolated are presented in Figures 3.1-3.30, 3.41. Spectral parameters for cations of the type $Co(AA)(ABA)X^{n+}$ are listed in Table 3.1, together with similar data for α and β-$Co(tetren)X^{n+}$, α-$Cr(tetren)Cl^{2+}$, $Co(NH_3)_5X^{n+}$ and $Cr(NH_3)_5Cl^{2+}$. The molar absorbancy index values, a_M, for each complex are within 3% for different preparations of salts that have similar infrared spectra characteristic of that particular complex.

The isomeric aquo cations were generated in solution from their chloro analogs by the addition of Hg^{2+} (as the acetate salt) in 0.1 F $HClO_4$. The Hg^{2+} catalysed hydrolysis was complete for all isomers after 18 hours at room temperature as evidenced by constant and reproducible

spectral parameters. Identical aquo cations were also generated from the chloro isomers by the addition of base (0.1 F NaOH) and then acidification with 3 F $HClO_4$ after 5 min. at room temperature.

The isomeric hydroxo cations were generated in solution from the chloro analogs by the addition of 0.1 F NaOH. The spectra of the resultant solutions were measured immediately.

Cobalt(III) in a regular octahedral site (O_h) has two absorption bands ascribed to the transitions $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$. Under a trigonal field the T_{1g} (O_h) level, which is the first excited state for low-spin Co(III), is split into levels with A_2 and E symmetry. Hence, the first absorption band ($^1A_{1g} \rightarrow {}^1T_{1g}$) splits into two overlapping optically active bands which are assigned the transitions $^1A_1 \rightarrow {}^1E_a$ and $^1A_1 \rightarrow {}^1A_2$. Whether the E state lies at a higher or lower energy than the A_2 state depends upon the arrangement of the ligands and their relative crystal field strengths. The longer wavelength band for (+)-$Co(en)_3^{3+}$ has been shown by a polarized circular dichroism spectrum of an oriented single crystal to correspond to the transition $^1A_1 \rightarrow {}^1E_a$.[70] In the acidopentaaminecobalt(III) complexes studied, the splitting of the long wavelength absorption is observed.

The $Co(AA)(ABA)X^{n+}$ complexes exhibit colours that are typical of cobalt(III) pentaamine complexes, viz. the chloro isomers have various shades of orange-red to violet, the bromo isomers are purple, the iodo isomers and green, the azido isomers are dark violet, the isothiocyanato, carboxylato, nitrato, hydroxo and aquo isomers are orange-red and the nitro isomers are yellow to orange.

There are some differences in the visible absorption spectra of the isomers obtained in each particular diamine-triamine system and this has been one of the means of establishing isomeric purity, but the main method of isomer characterisation has been through infrared spectra.

(2) Optical Rotatory Dispersion (ORD) Spectra

The ORD spectra of (-)-D-$Co(pn)(dien)Cl^{2+}$, (+)-XI-$Co(Nip\text{-}ibn)(dien)Cl^{2+}$, (-)-d-$Co(tmd)(dien)Cl^{2+}$, (+)-I-$Co(Me\text{-}tmd)(dien)Cl^{2+}$ and (+)-V-$Co(Me\text{-}tmd)(dien)Cl^{2+}$ together with their visible absorption spectra are presented in Figures 3.31-3.35, respectively.

These ORD spectra have been used only as an aid for structural assignment and no attempt has been made in assigning absolute configurations to these complexes.

The magnitudes of the ORD spectra of (+)-XI-$Co(Nip\text{-}ibn)(dien)Cl^{2+}$ and of (+)-I-$Co(Me\text{-}tmd)(dien)Cl^{2+}$ are small and this indicates either that only the asymmetric nitrogen centres in these complexes have been resolved, or the

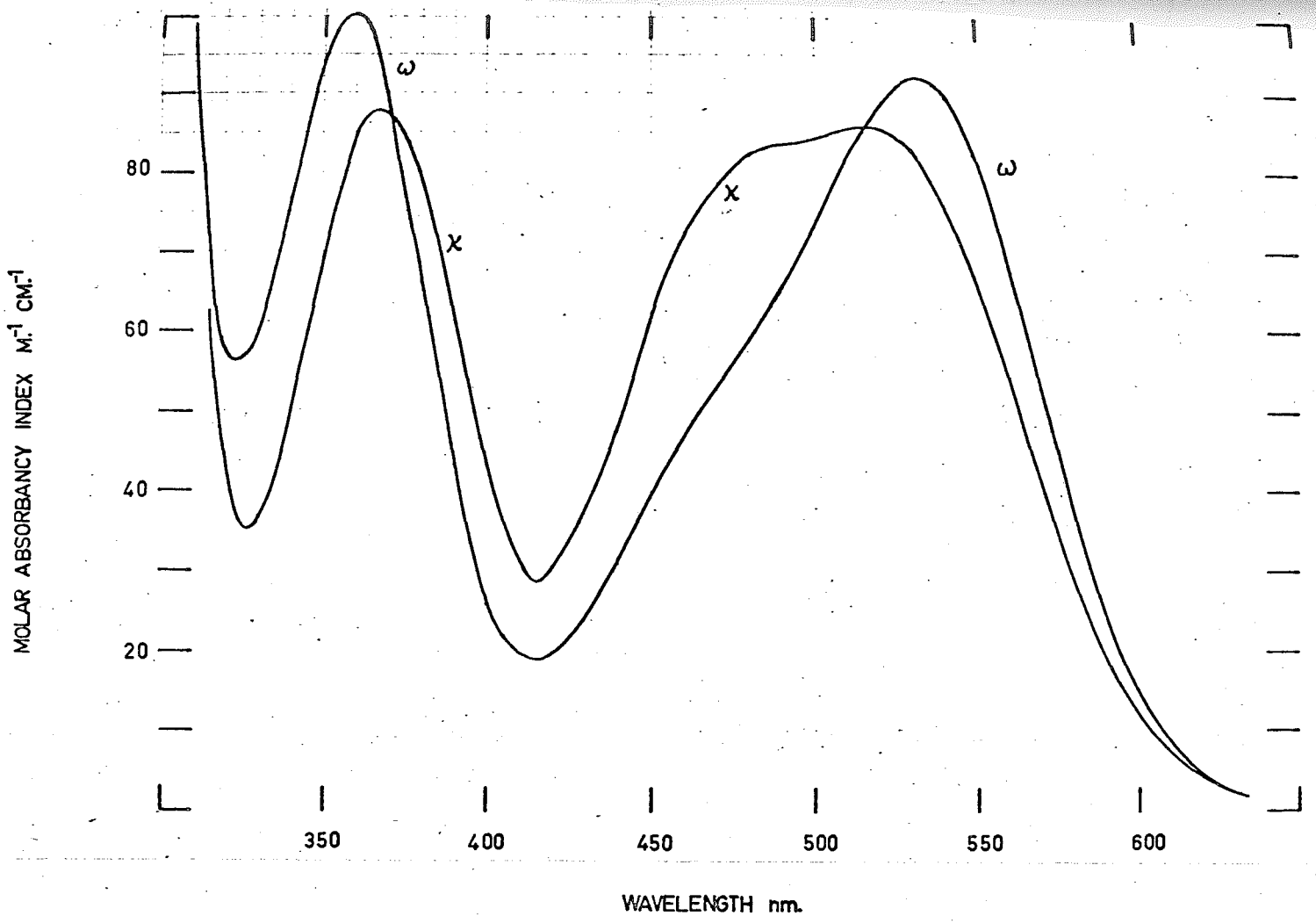


Figure 3.1 Visible absorption spectra of χ and ω - $Co(en)(dien)Cl^{2+}$ in 0.1 F $HClO_4$ at 20-25°.

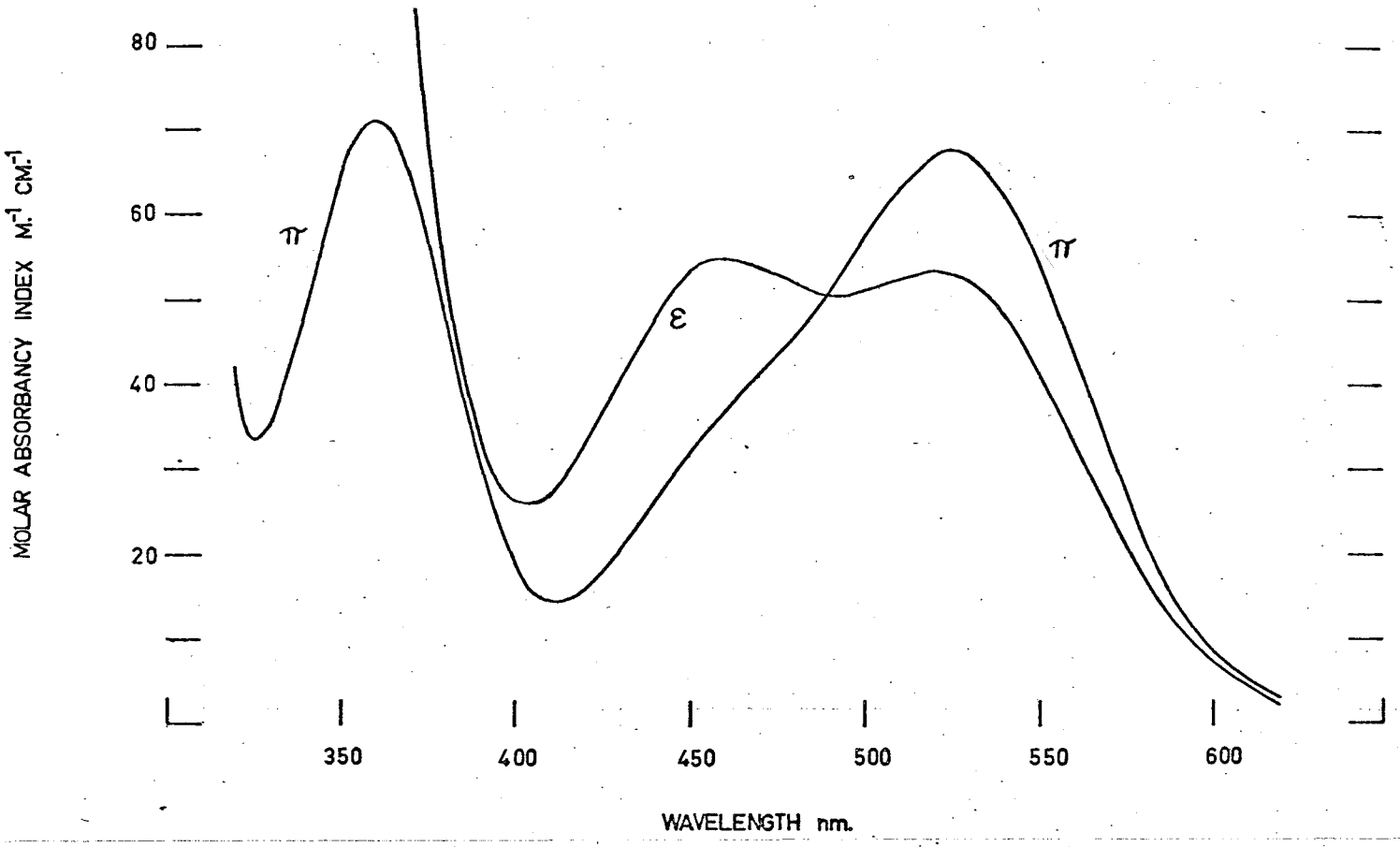


Figure 3.2 Visible absorption spectra of π and "ε" - $Co(en)(dien)Cl^{2+}$ in 0.1 F $HClO_4$ at 20-25°.

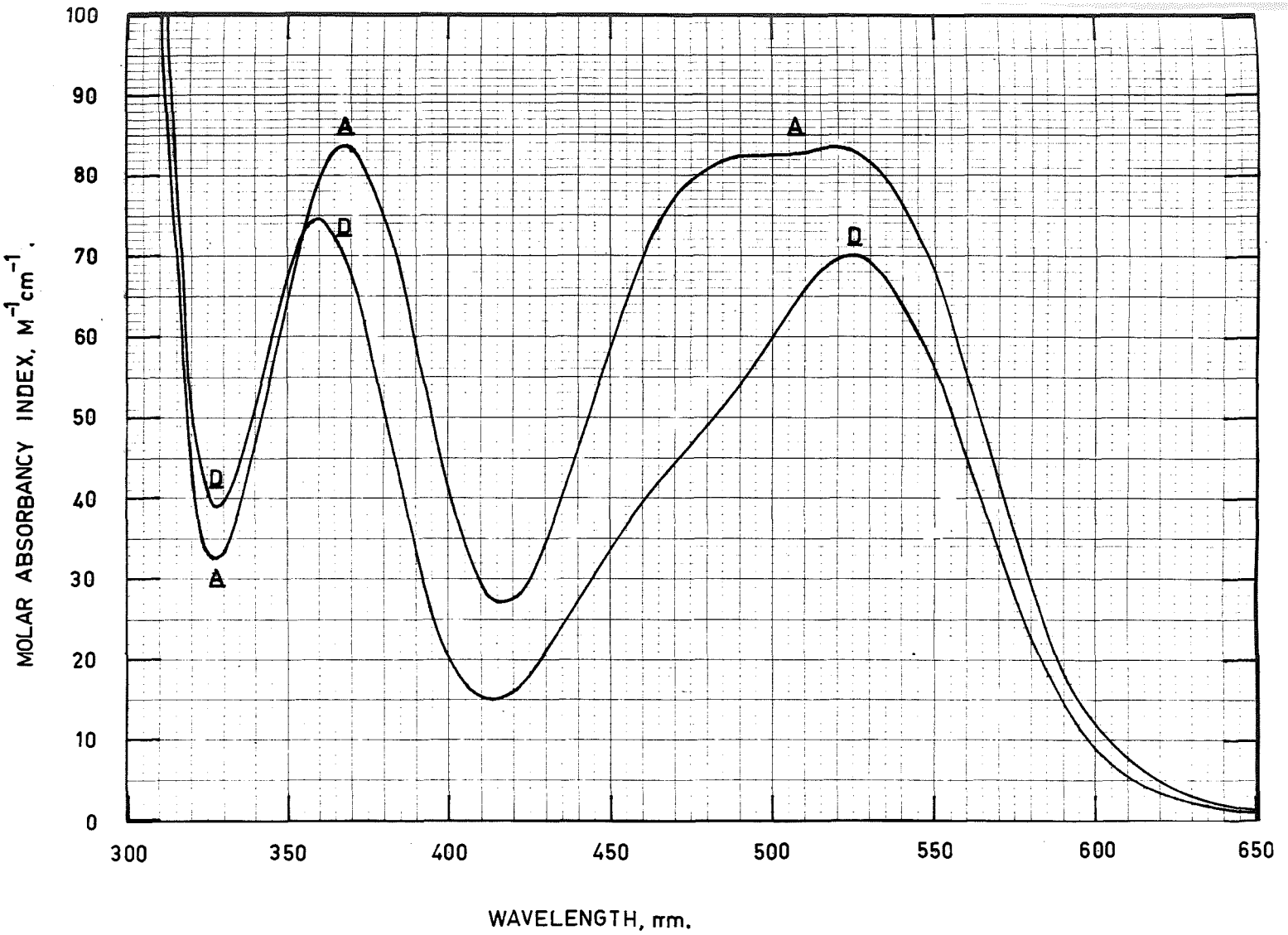


Figure 3.3 Visible absorption spectra of A and D - $Co(pn)(dien)Cl^{2+}$ in 0.1 F $HClO_4$ at 20-25°.

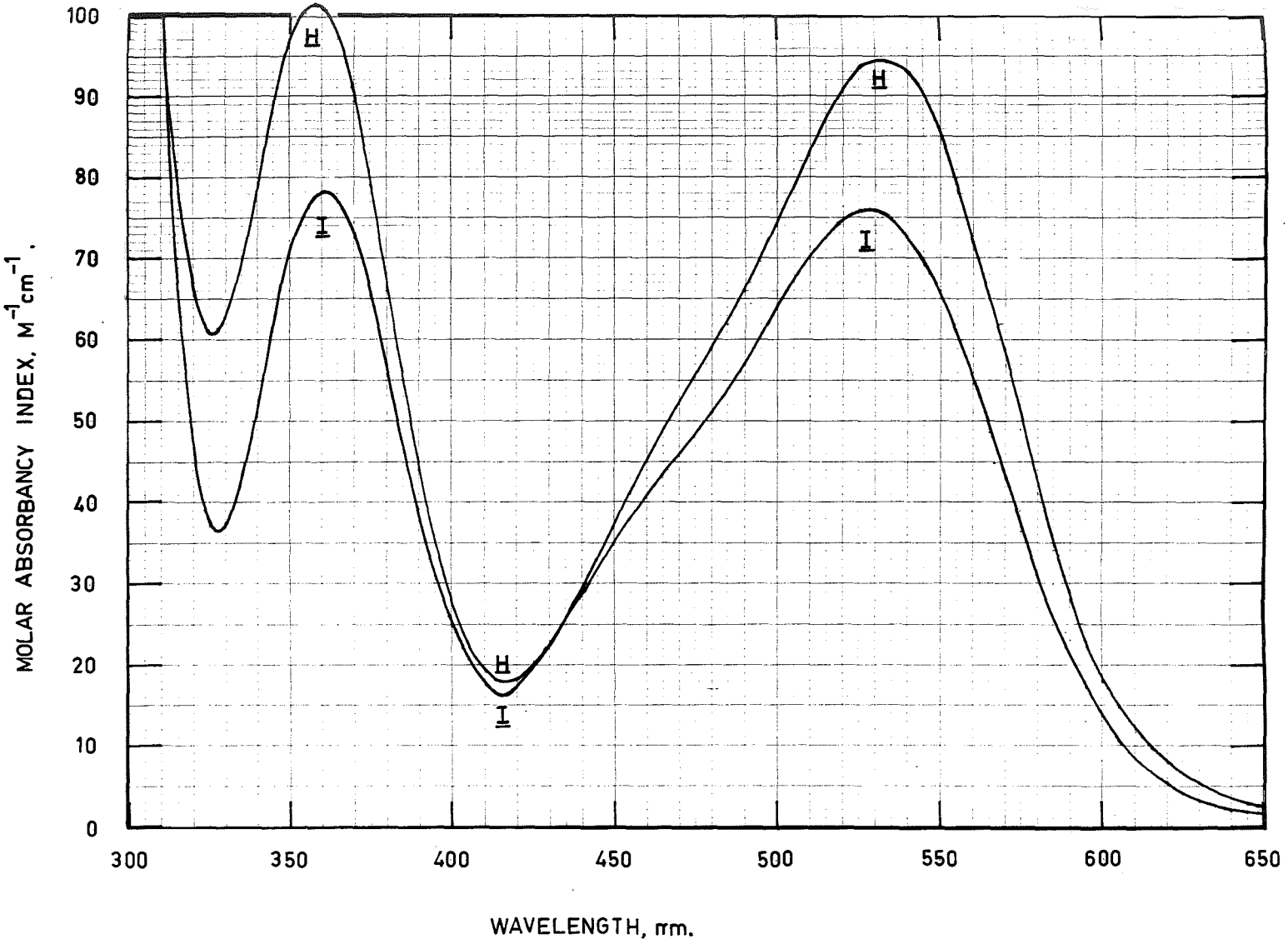


Figure 3.4 Visible absorption spectra of H and I - $Co(pn)(dien)Cl^{2+}$ in 0.1 F $HClO_4$ at 20-25°.

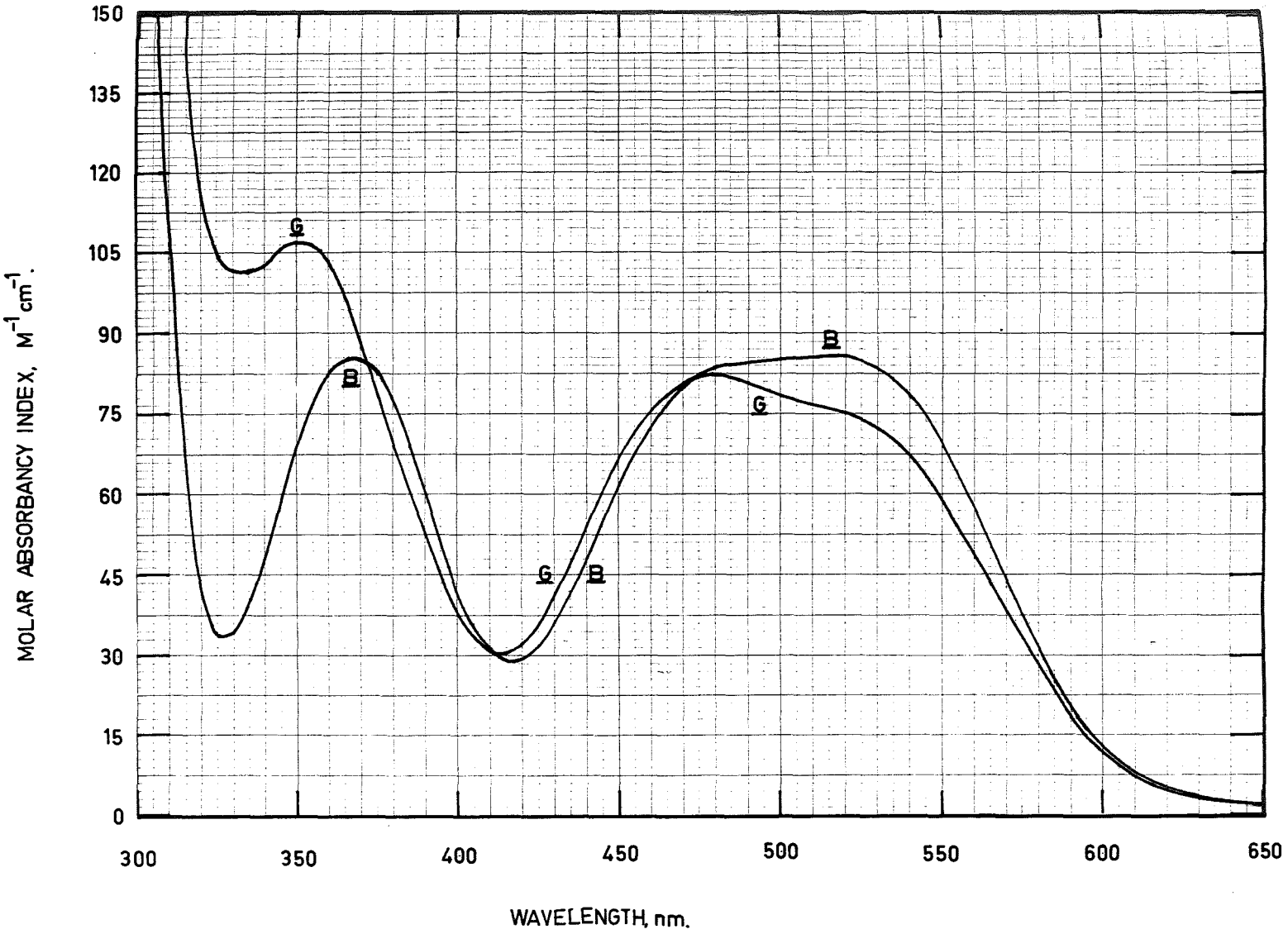


Figure 3.5 Visible absorption spectra of B and G - $Co(pn)(dien)Cl^{2+}$ in 0.1 F $HClO_4$ at 20-25°.

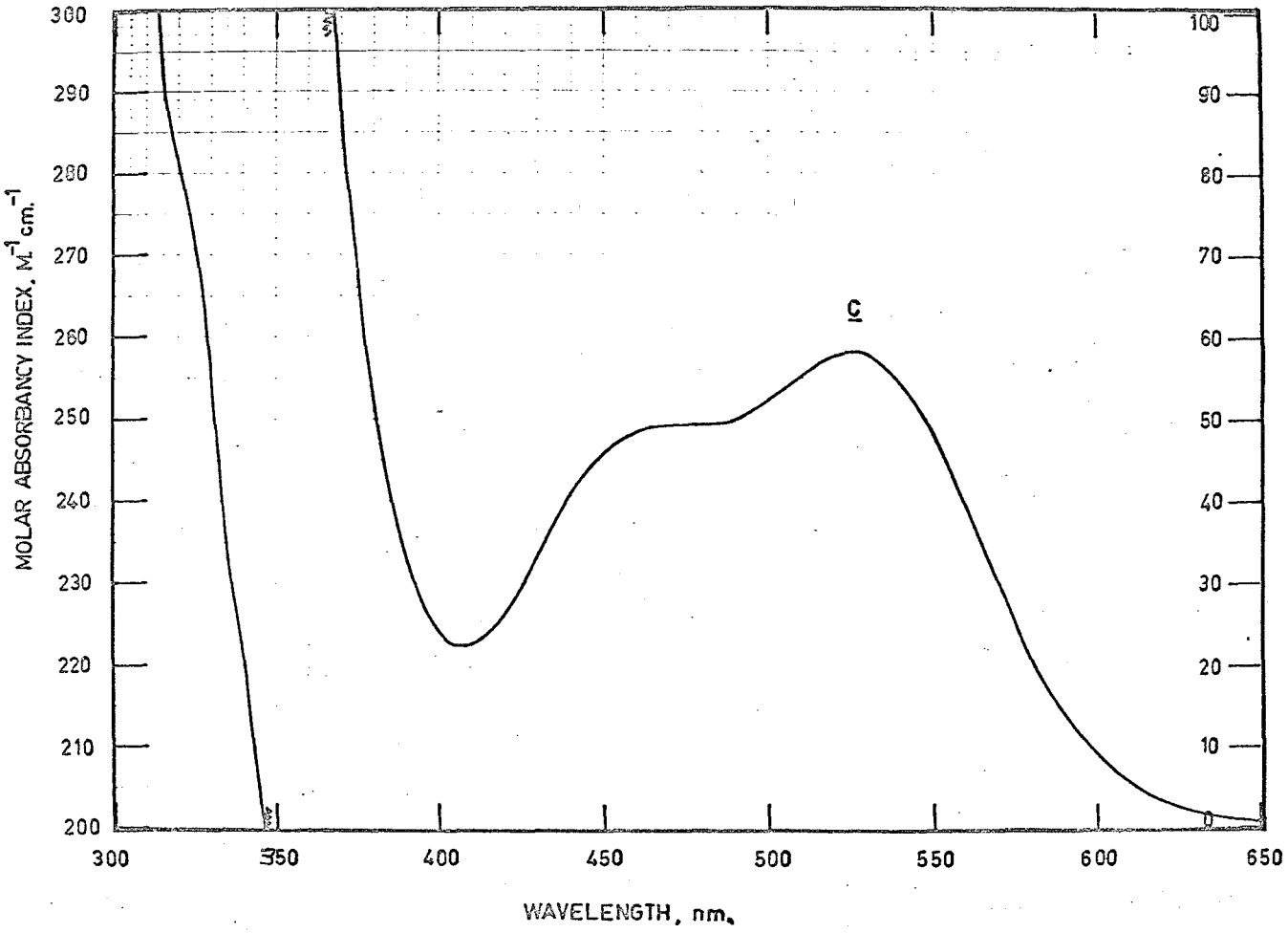


Figure 3.6 Visible absorption spectrum of C - $Co(pn)(dien)Cl^{2+}$ in 0.1 F $HClO_4$ at 20-25°.

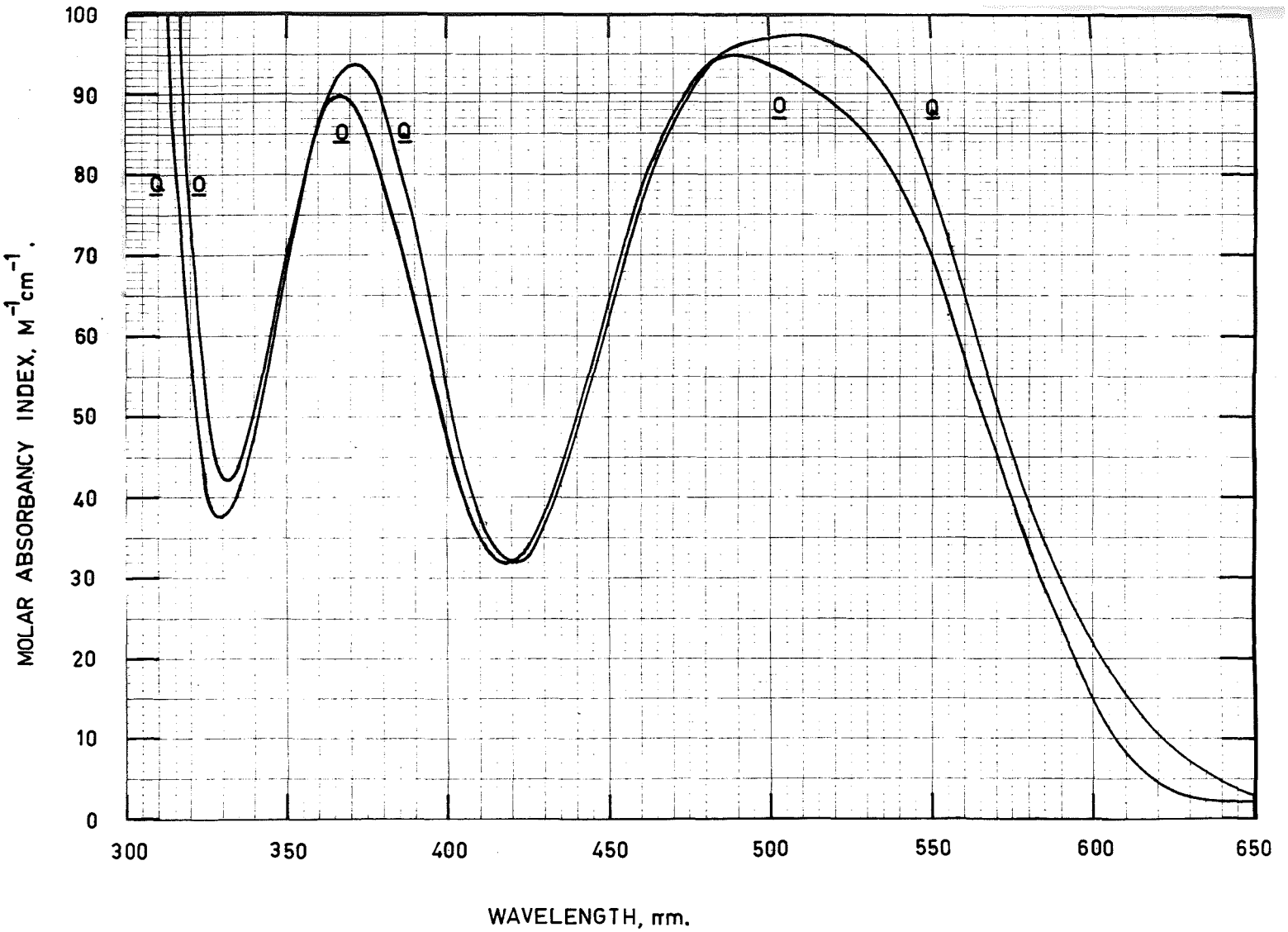


Figure 3.7 Visible absorption spectra of O and Q - $Co(ibn)(dien)Cl^{2+}$ in 0.1 F $HClO_4$ at 20-25°.

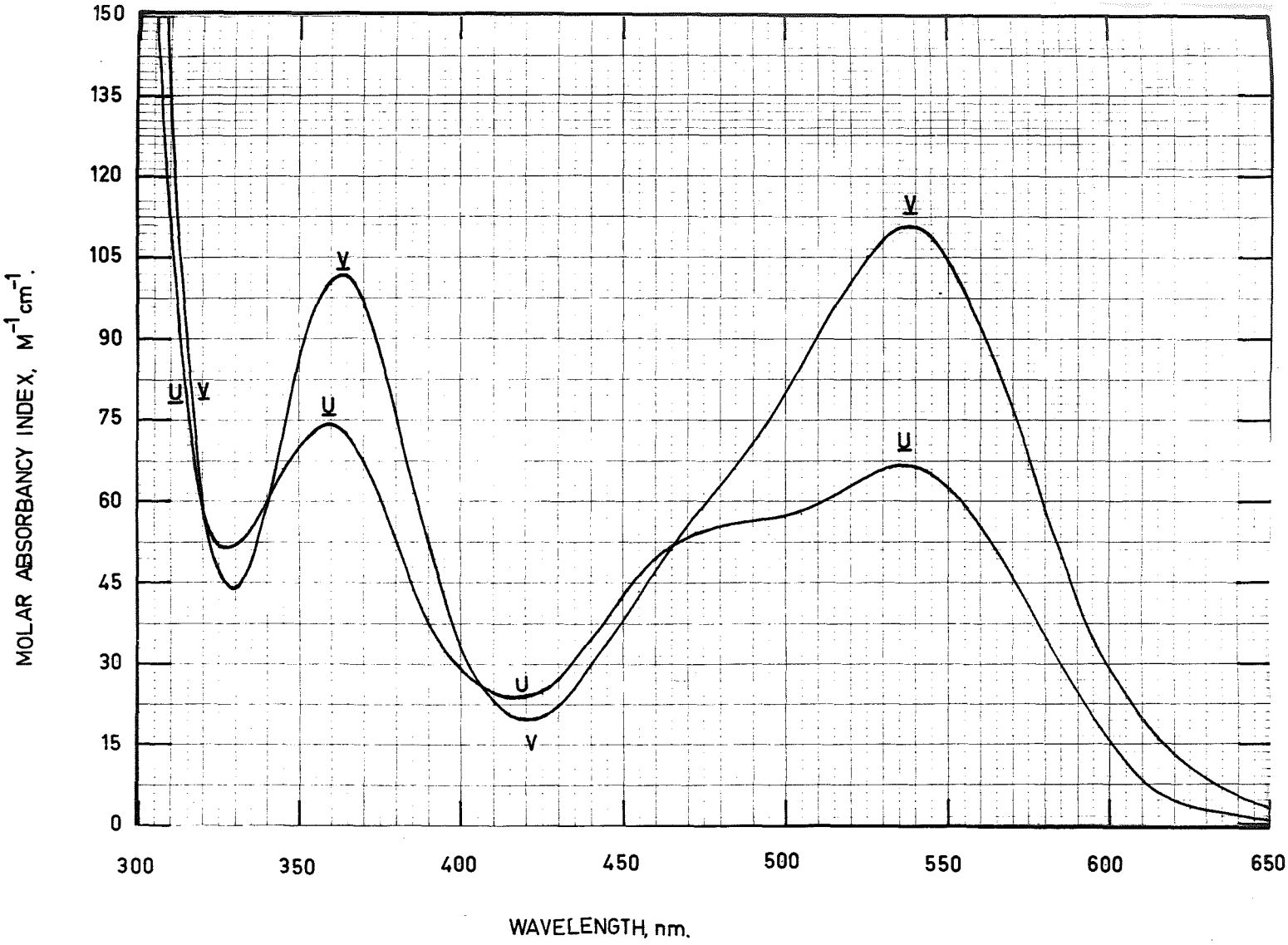


Figure 3.8 Visible absorption spectra of U and V - $Co(ibn)(dien)Cl^{2+}$ in 0.1 F $HClO_4$ at 20-25°.

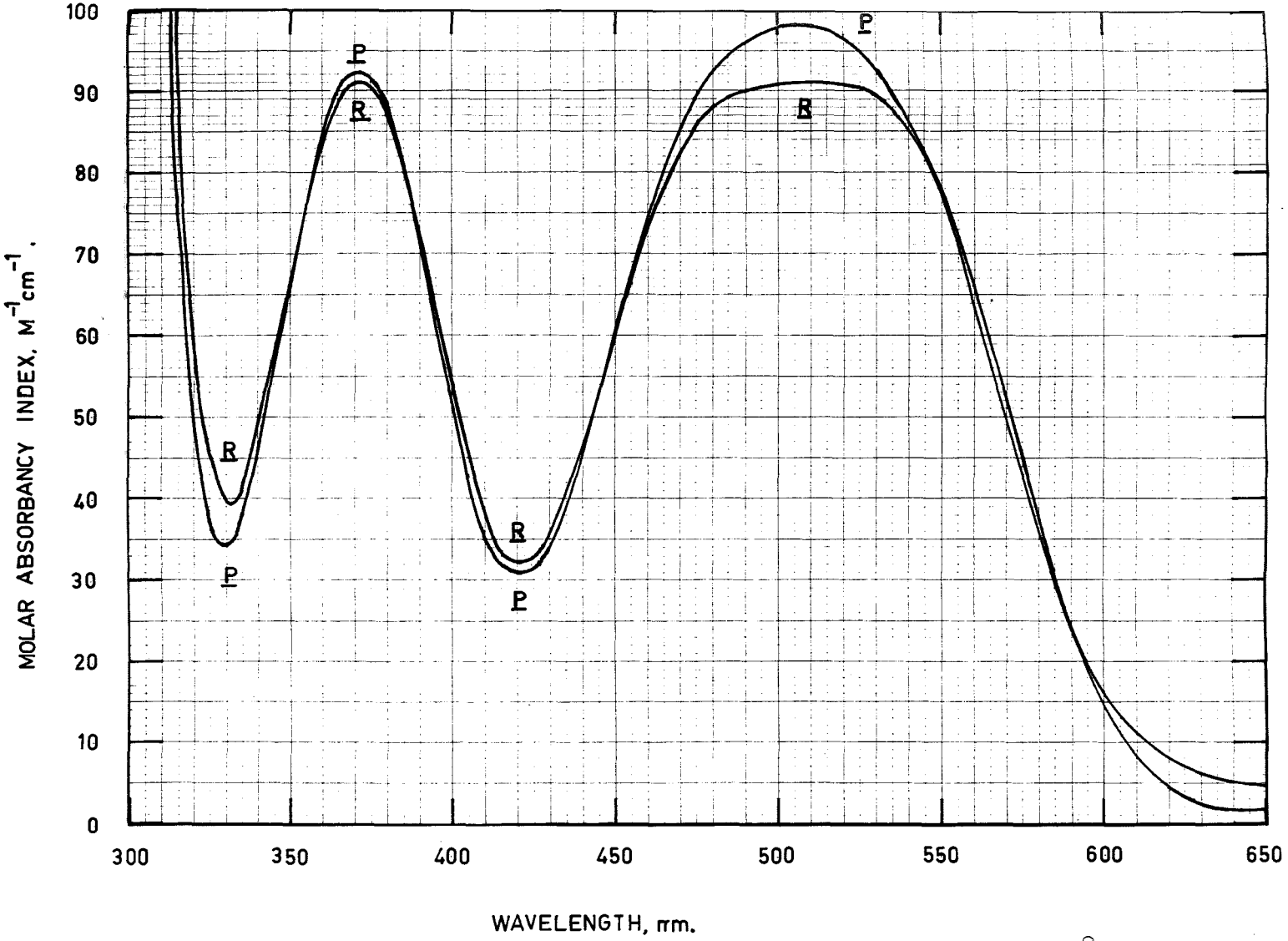


Figure 3.9 Visible absorption spectra of P and R - $Co(ibn)(dien)Cl^{2+}$ in 0.1 F $HClO_4$ at 20-25°.

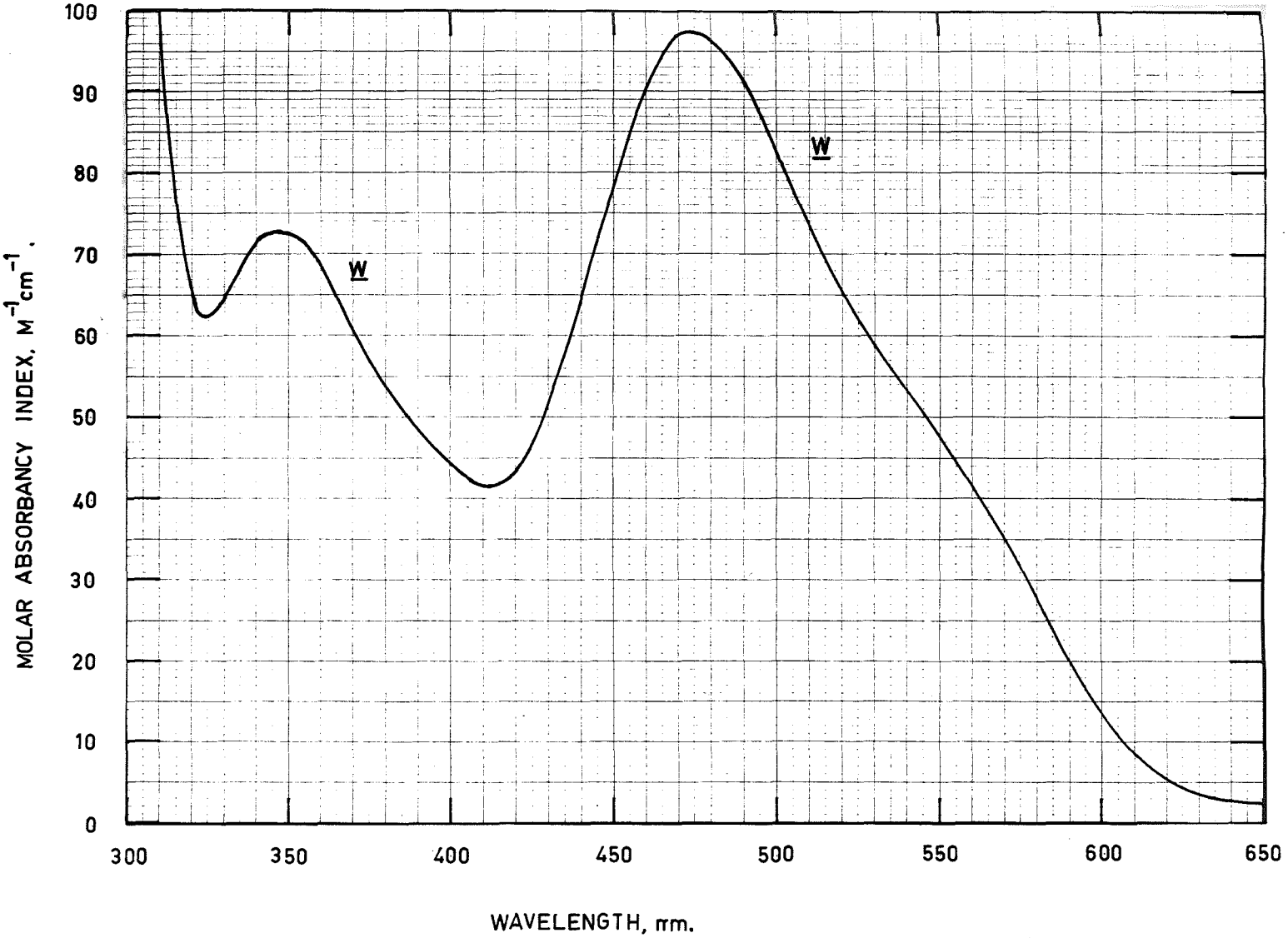


Figure 3.10 Visible absorption spectrum of W - $Co(ibn)(dien)Cl^{2+}$ in 0.1 F $HClO_4$ at 20-25°.

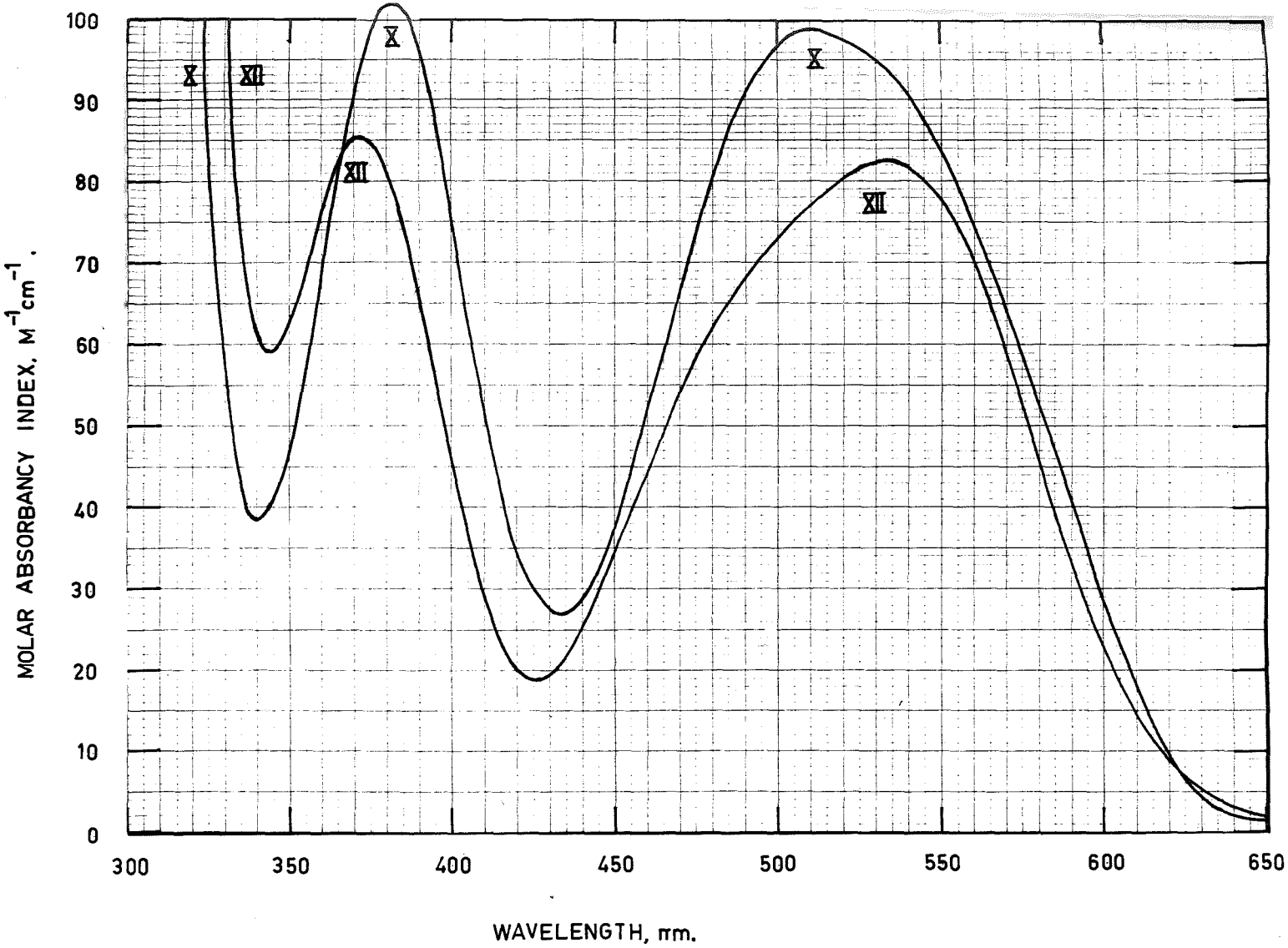


Figure 3.11 Visible absorption spectra of X and XII - $Co(Nip\text{-}ibn)(dien)Cl^{2+}$ in 0.1 F $HClO_4$ at 20-25°.

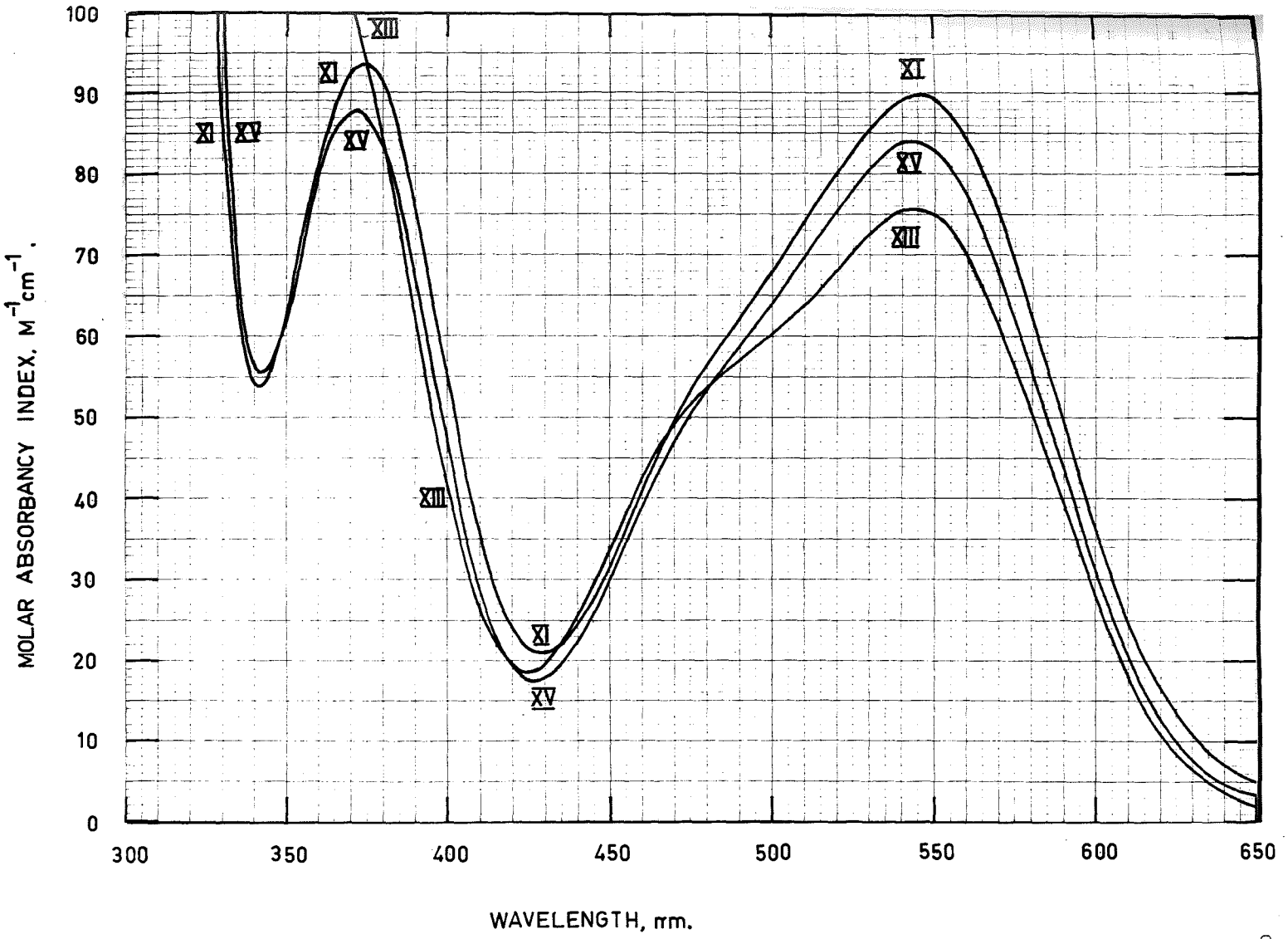


Figure 3.12 Visible absorption spectra of XI, XIII and XV - $Co(Nip\text{-}ibn)(dien)Cl^{2+}$ in 0.1 F $HClO_4$ at 20-25°.

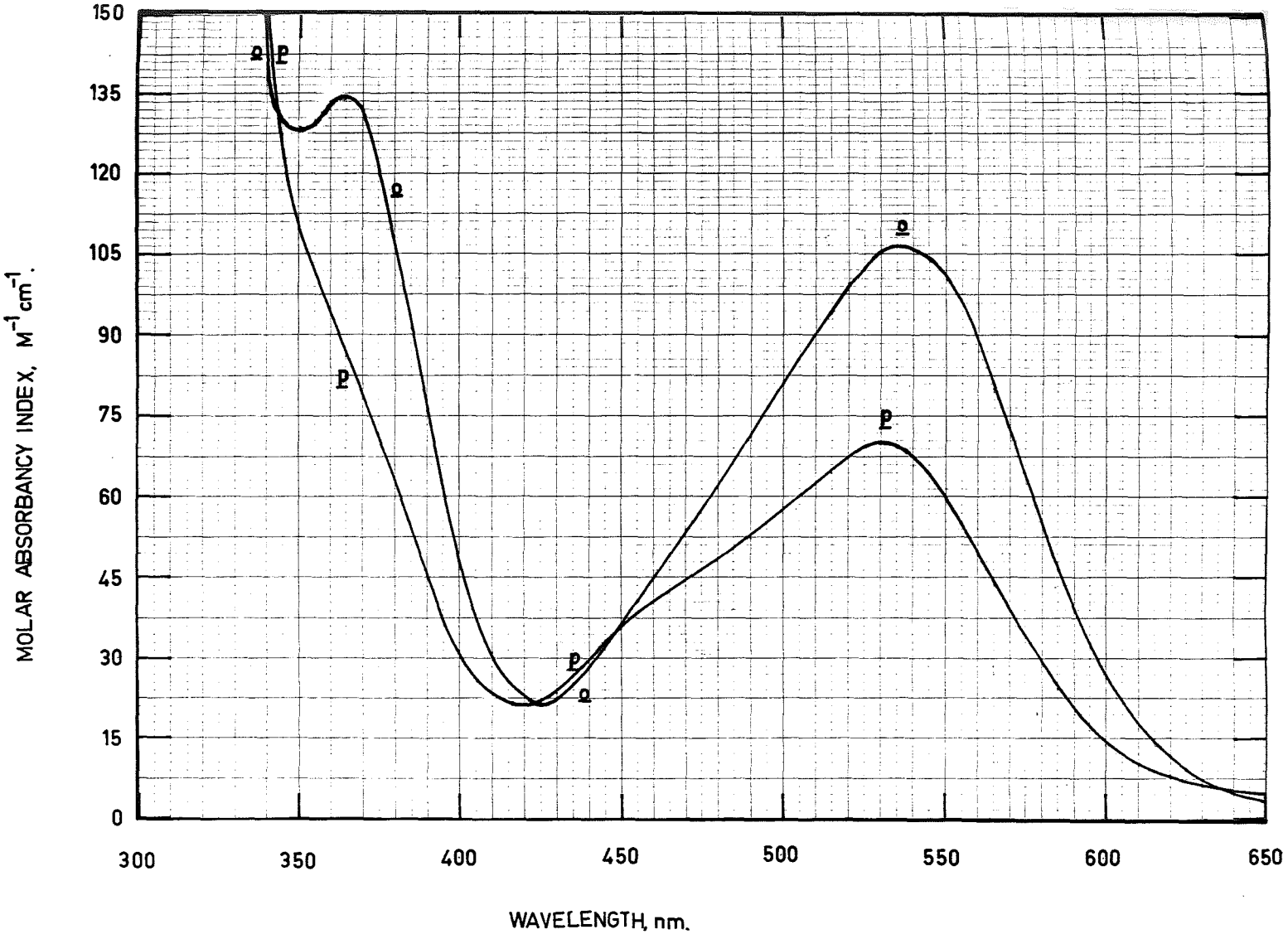


Figure 3.13 Visible absorption spectra of o and p - $Co(stien)(dien)Cl^{2+}$ in 0.1 F $HClO_4$ at 20-25°.

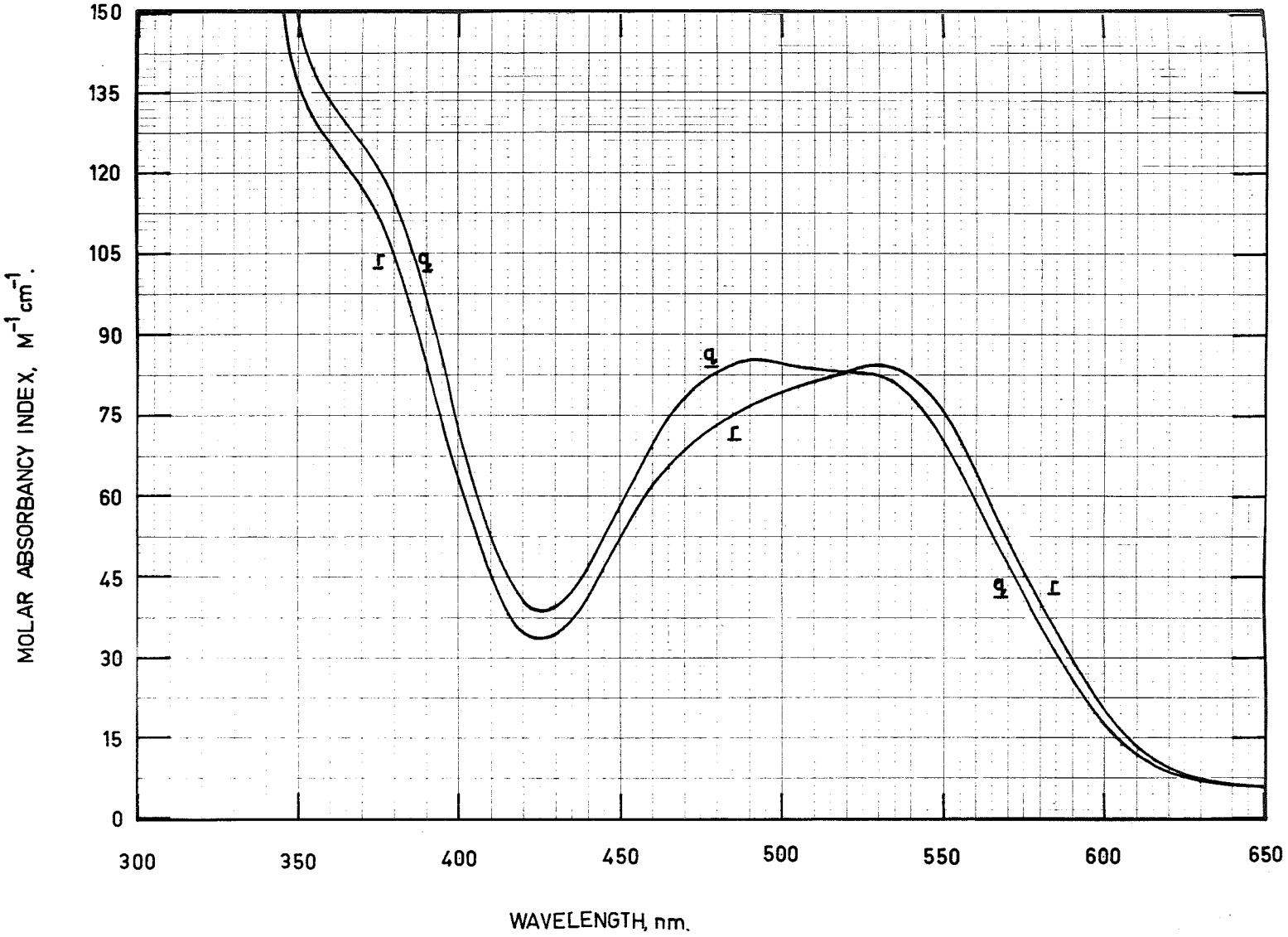


Figure 3.14 Visible absorption spectra of q and r - $Co(stien)(dien)Cl^{2+}$ in 0.1 F $HClO_4$ at 20-25°.

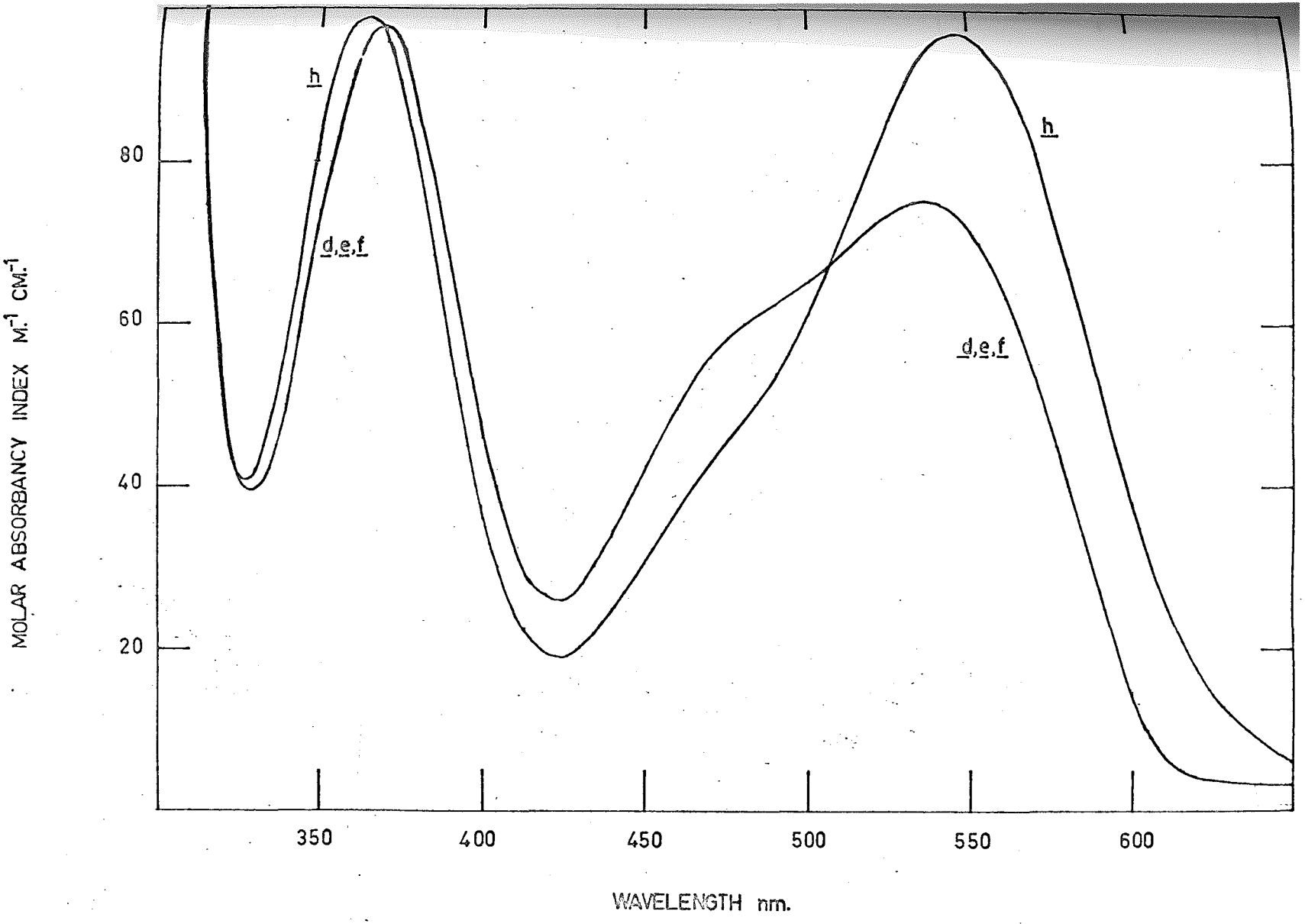


Figure 3.15 Visible absorption spectra of d, e, f and h - $Co(tmd)(dien)Cl^{2+}$ in 0.1 F $HClO_4$ at 20-25°.

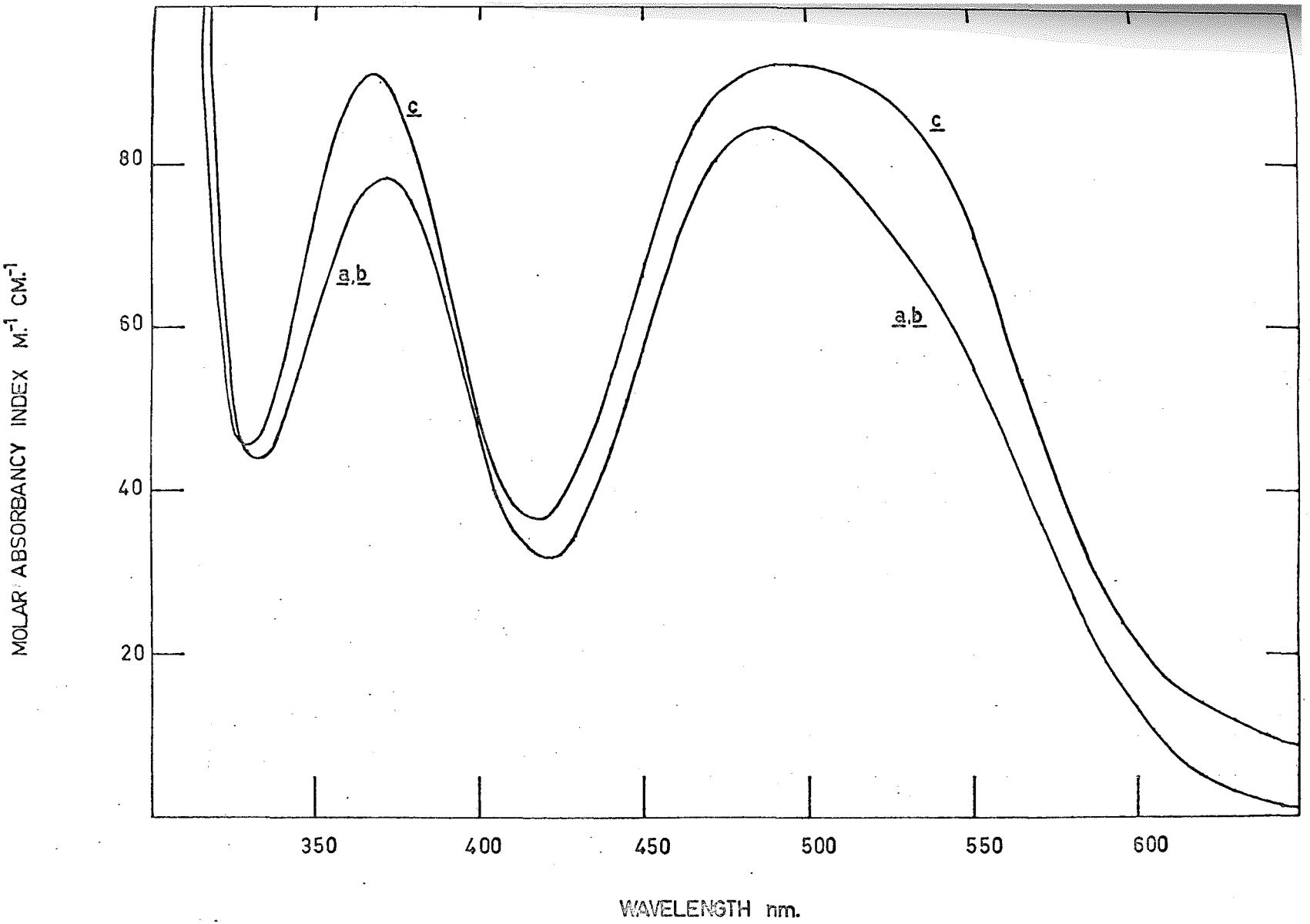


Figure 3.16 Visible absorption spectra of a, b and c - $Co(tmd)(dien)Cl^{2+}$ in 0.1 F $HClO_4$ at 20-25°.

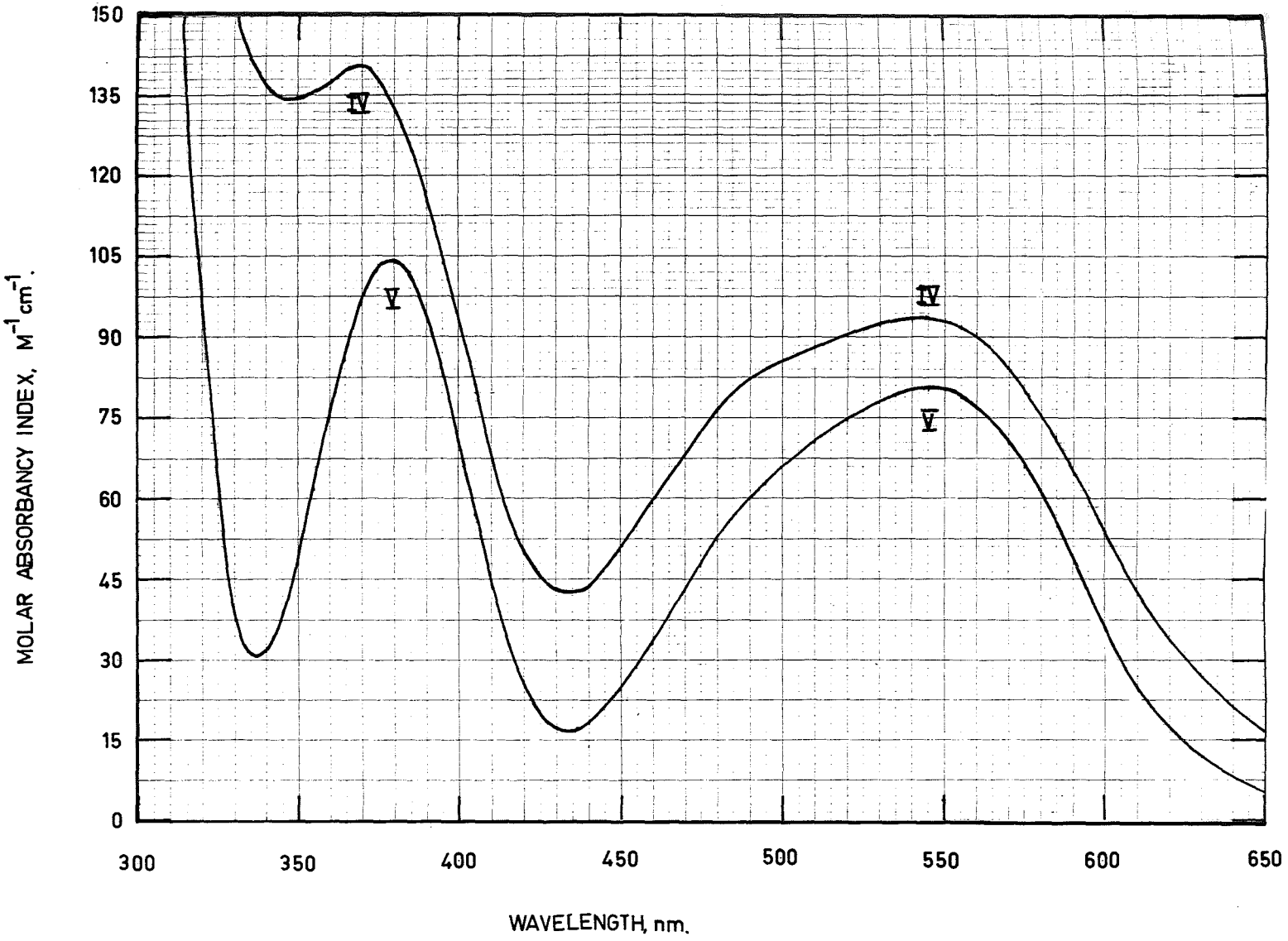


Figure 3.17 Visible absorption spectra of IV and V - $Co(Me\text{-}tmd)(dien)Cl^{2+}$ in 0.1 F $HClO_4$ at 20-25°.

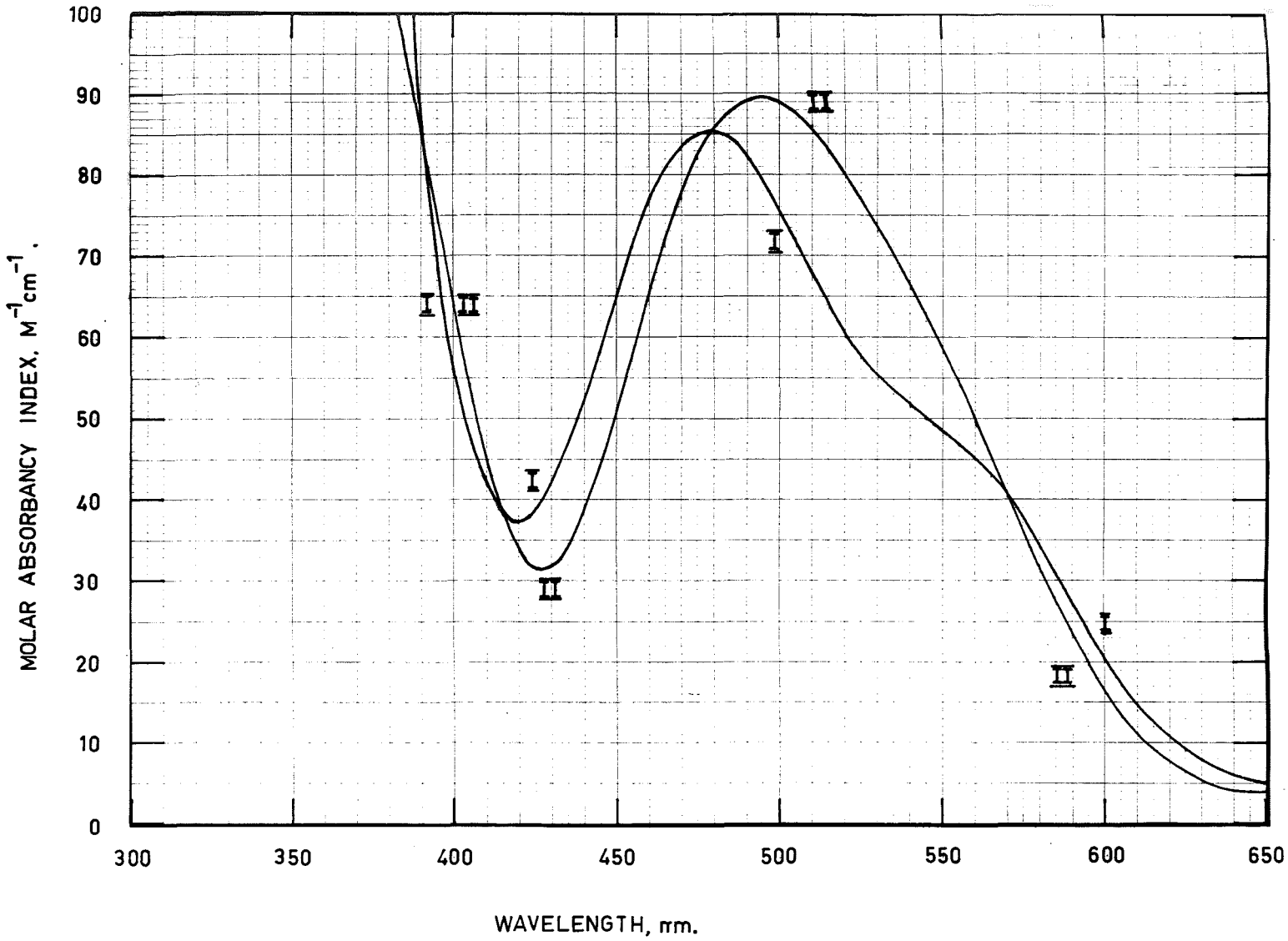


Figure 3.18 Visible absorption spectra of I and II - $Co(Me\text{-}tmd)(dien)Cl^{2+}$ in 0.1 F $HClO_4$ at 20-25°.

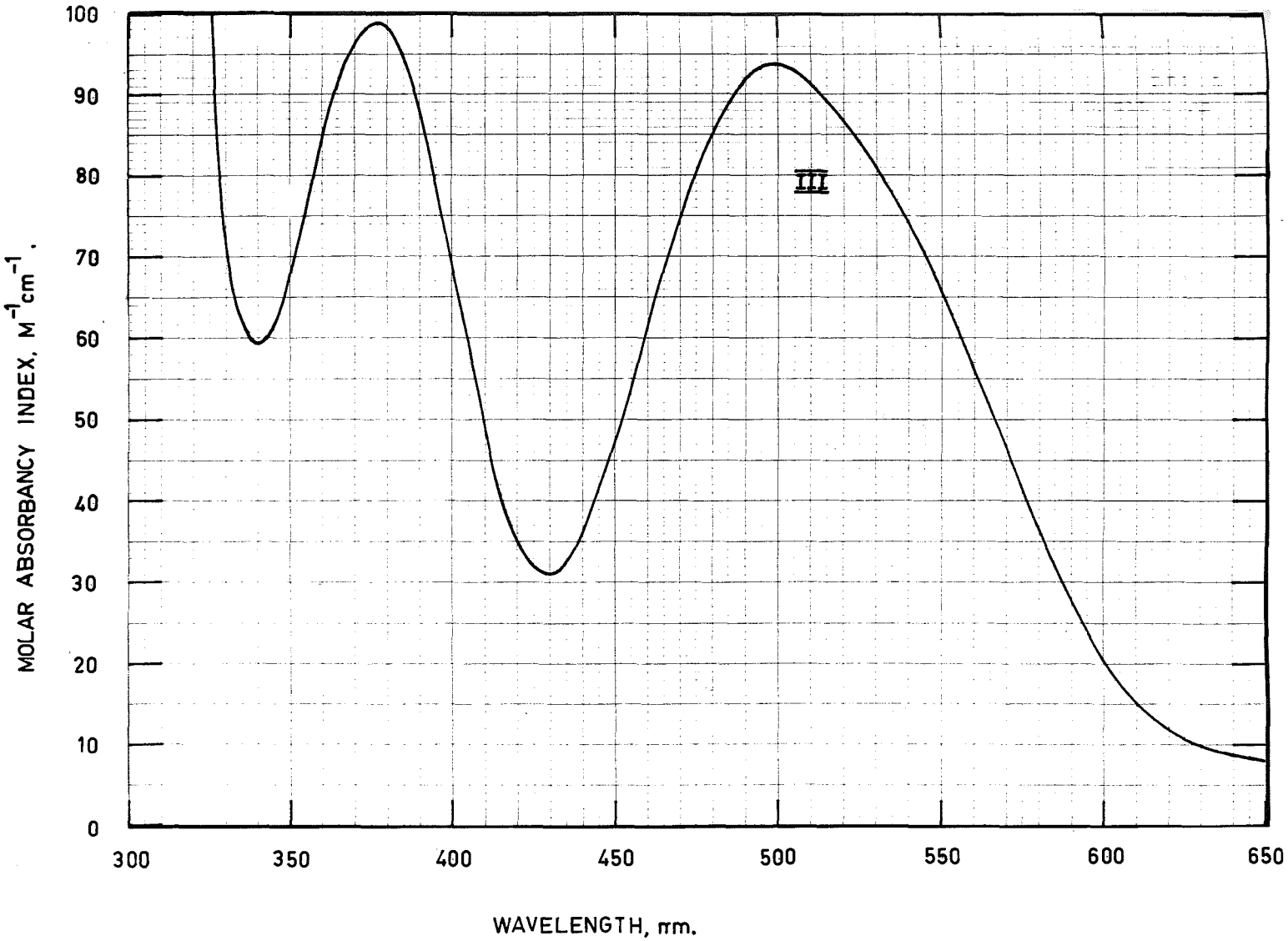


Figure 3.19 Visible absorption spectrum of III - $Co(Me\text{-}tmd)(dien)Cl^{2+}$ in 0.1 F $HClO_4$ at 20-25°.

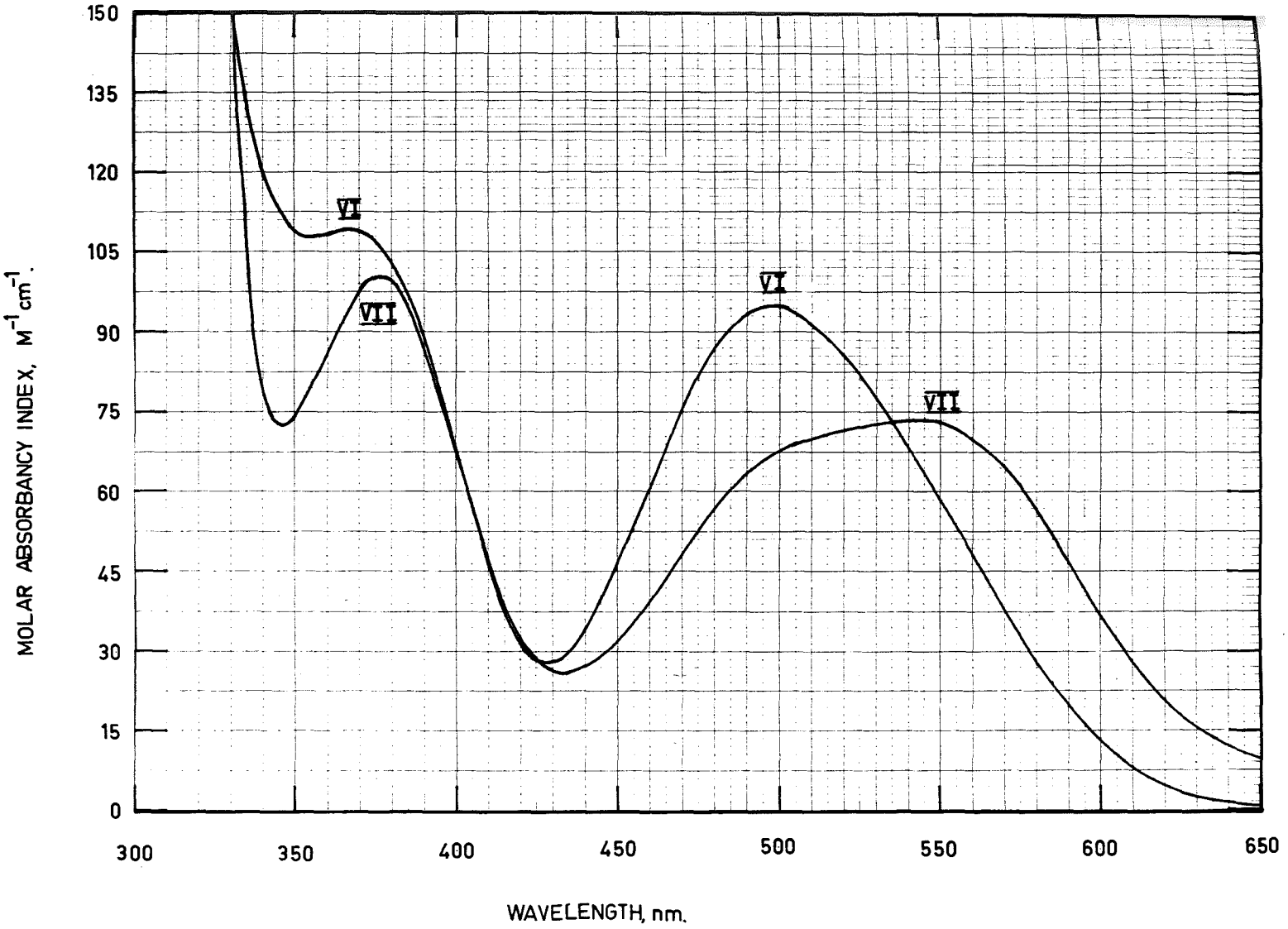


Figure 3.20 Visible absorption spectra of VI and VII - $Co(Bu\text{-}tmd)(dien)Cl^{2+}$ in 0.1 F $HClO_4$ at 20-25°.

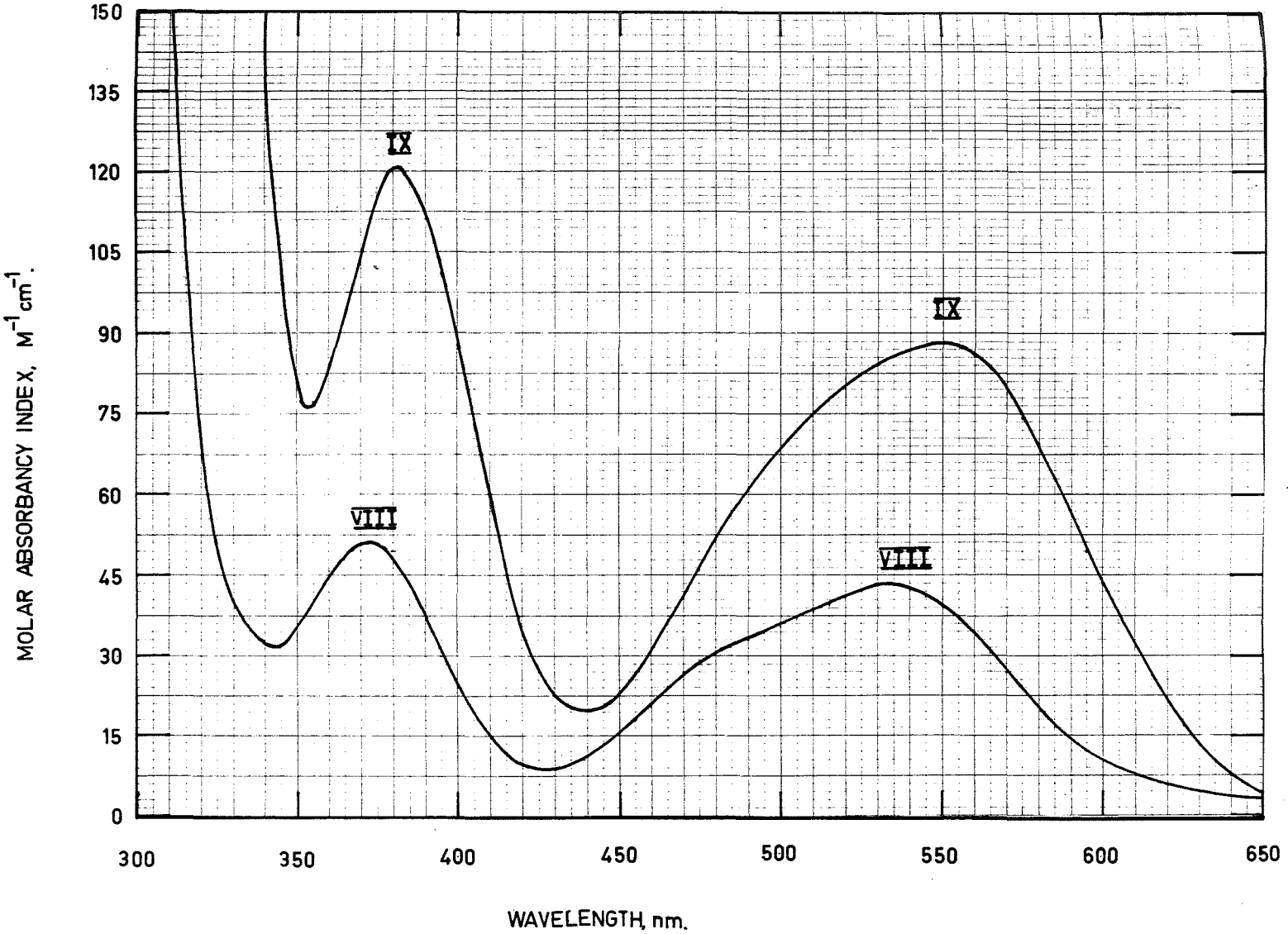


Figure 3.21 Visible absorption spectra of VIII and IX - $Co(tmd\text{-}hex)(dien)Cl^{2+}$ in 0.1 M $HClO_4$ at 20-25°.

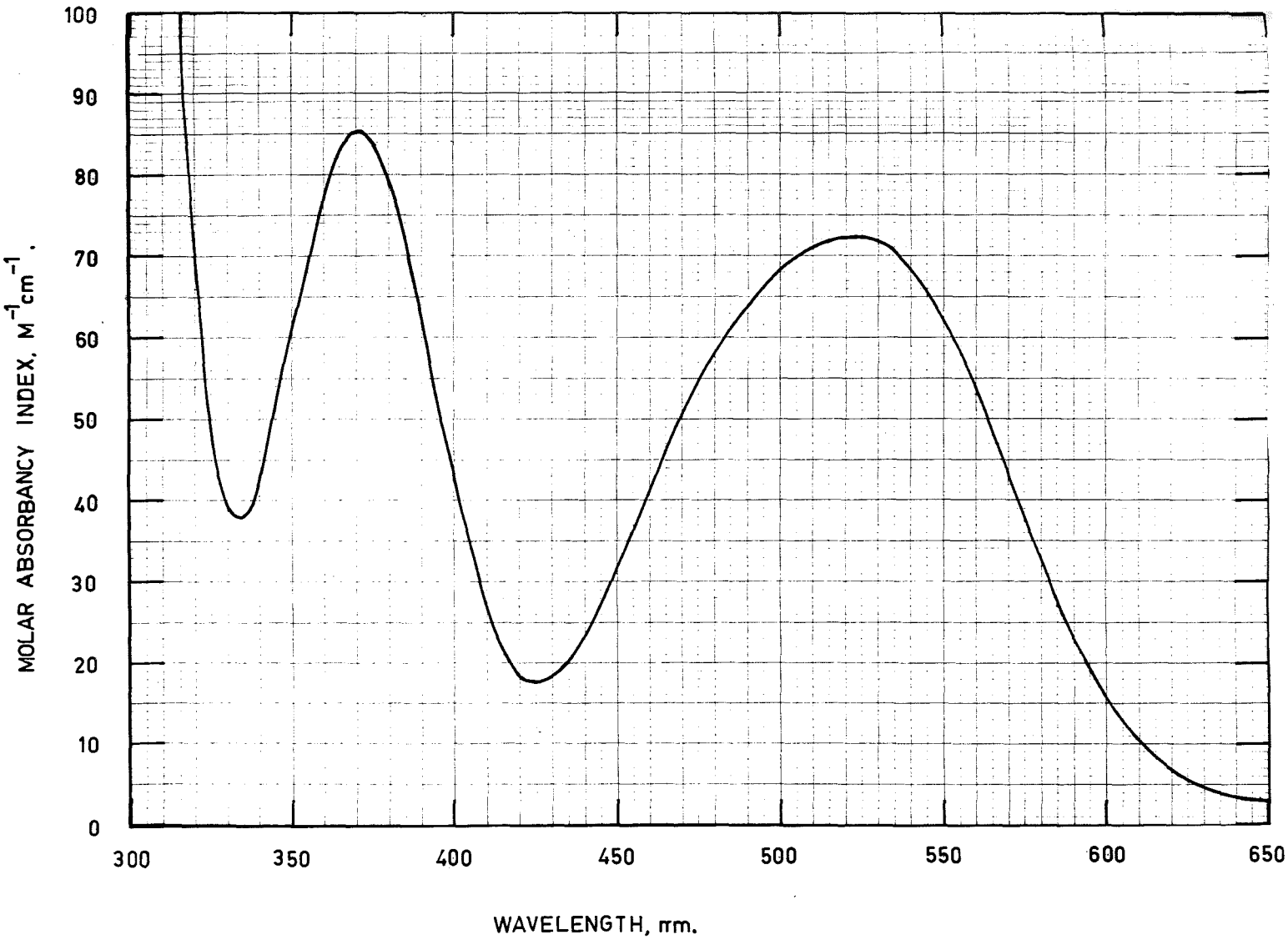


Figure 3.22 Visible absorption spectrum of 1 - $Co(1,4\text{-bn})(dien)Cl^{2+}$ in 0.1 F $HClO_4$ at 20-25°.

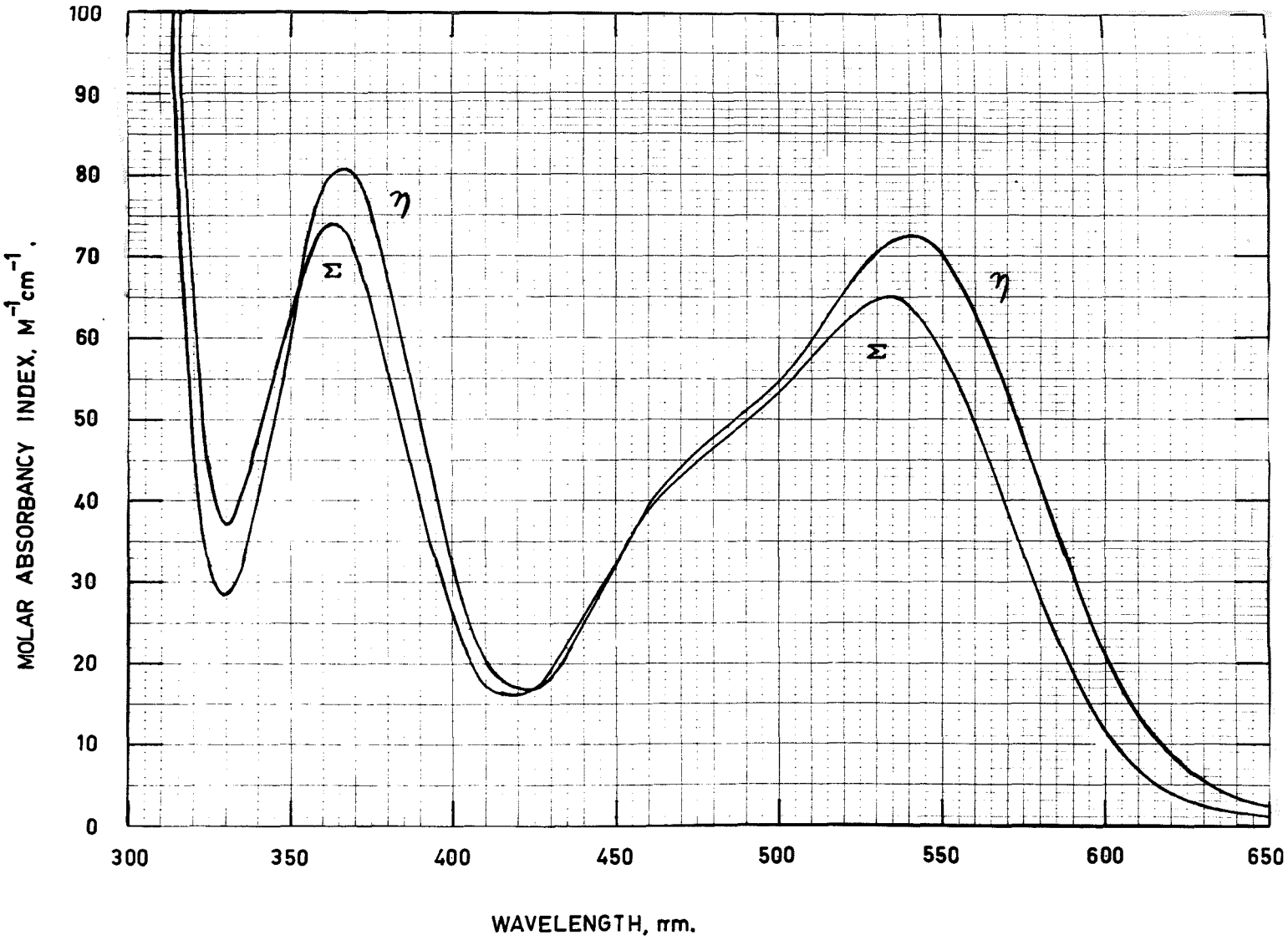


Figure 3.23 Visible absorption spectra of Σ and η - $Co(2,3\text{-tri})(en)Cl^{2+}$ in 0.1 F $HClO_4$ at 20-25° .

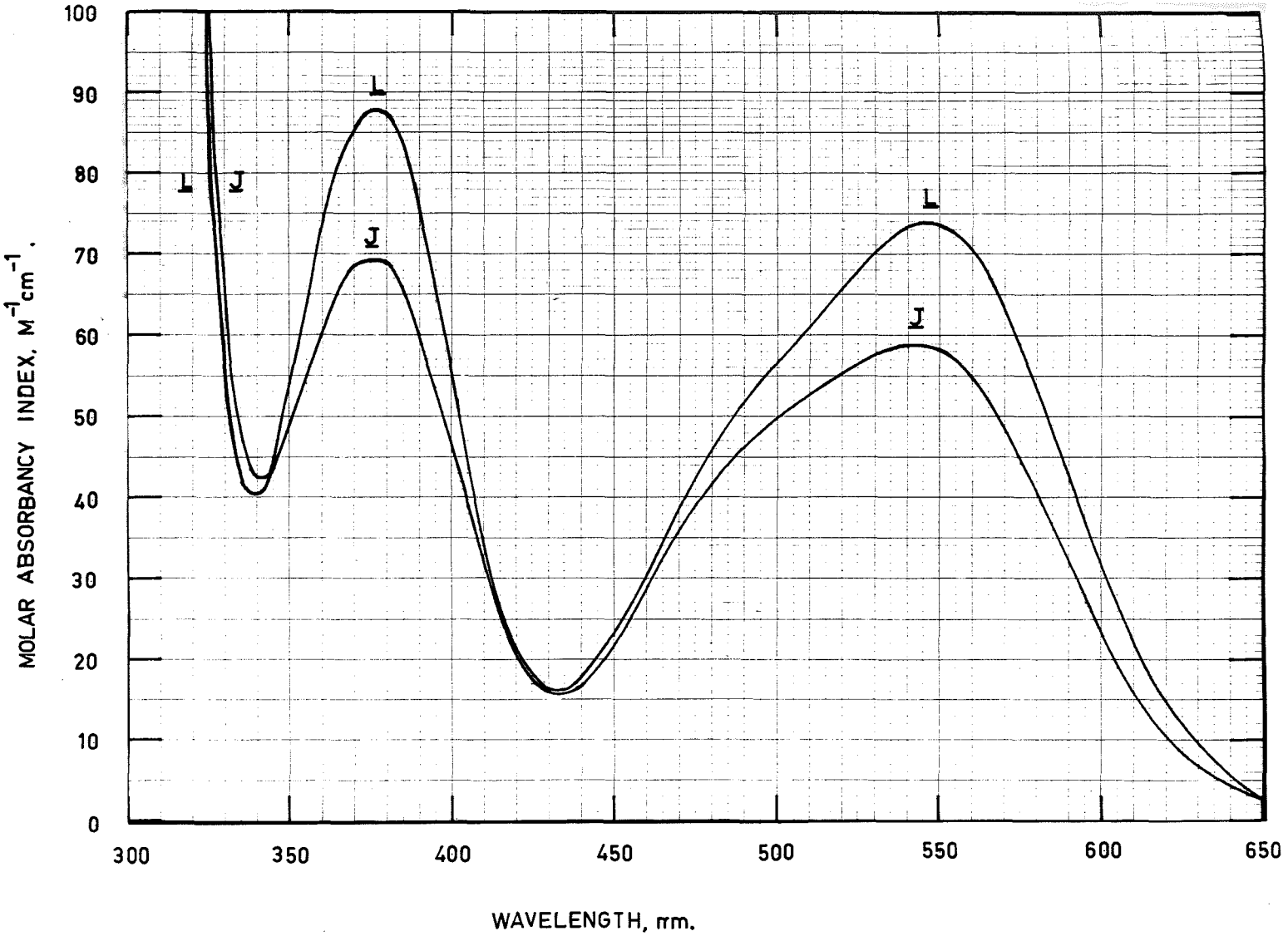


Figure 3.24 Visible absorption spectra of J and L - $Co(pn)(dpt)Cl^{2+}$ in 0.1 F $HClO_4$ at 20-25°.

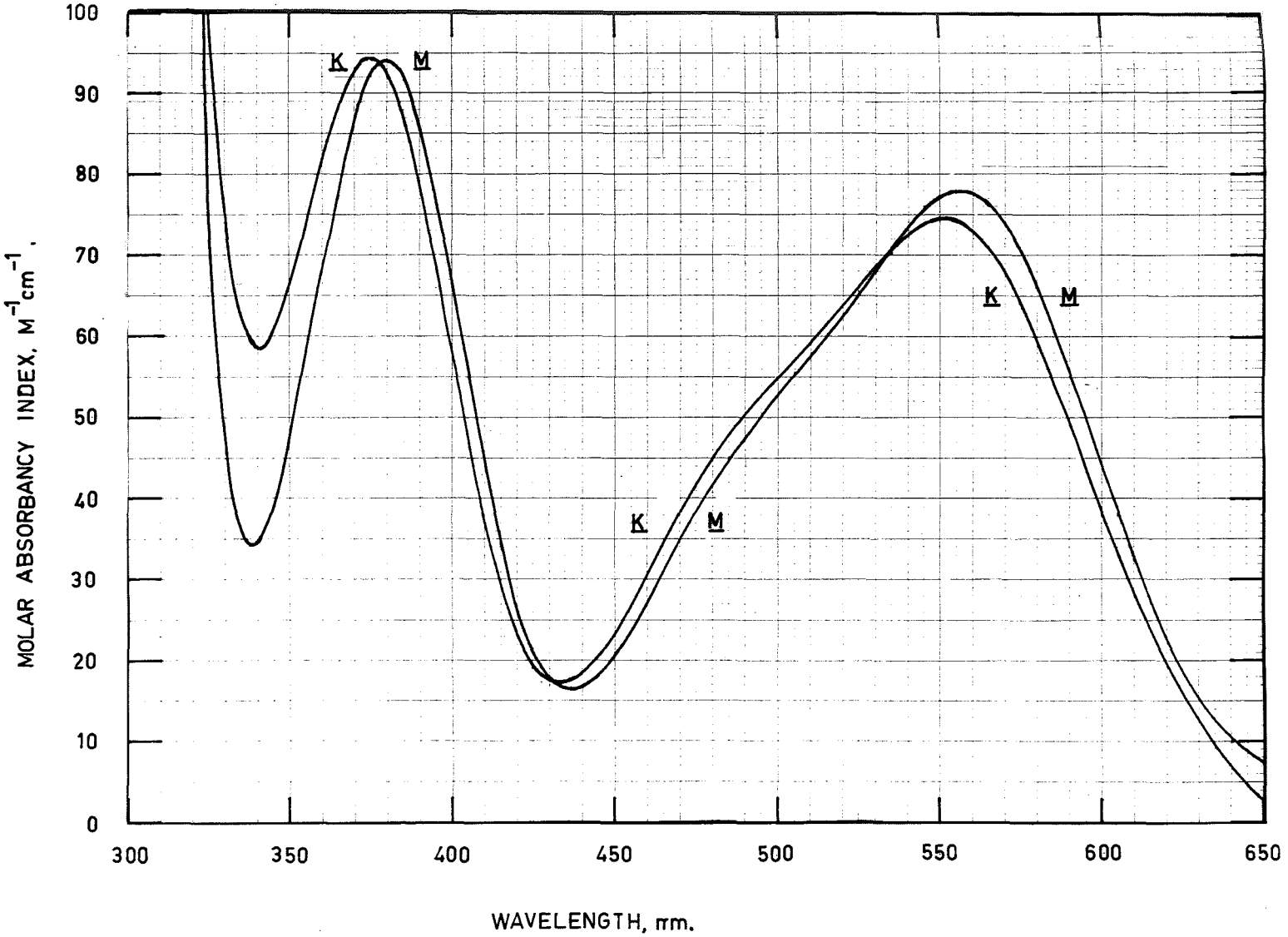


Figure 3.25 Visible absorption spectra of K and M - $Co(pn)(dpt)Cl^{2+}$ in 0.1 F $HClO_4$ at 20-25°.

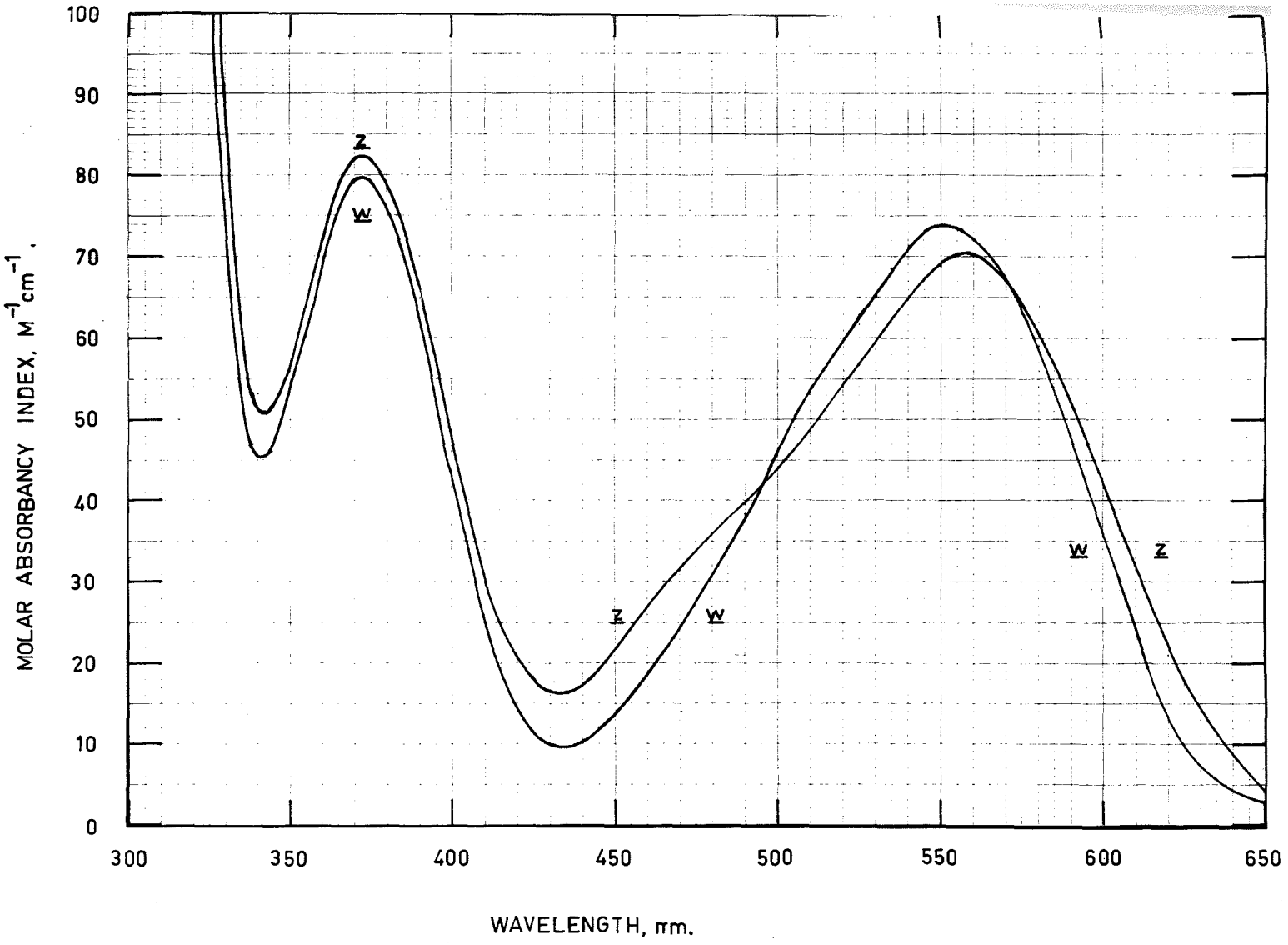


Figure 3.26 Visible absorption spectra of w and z - $Co(ibn)(dpt)Cl^{2+}$ in 0.1 F $HClO_4$ at 20-25°.

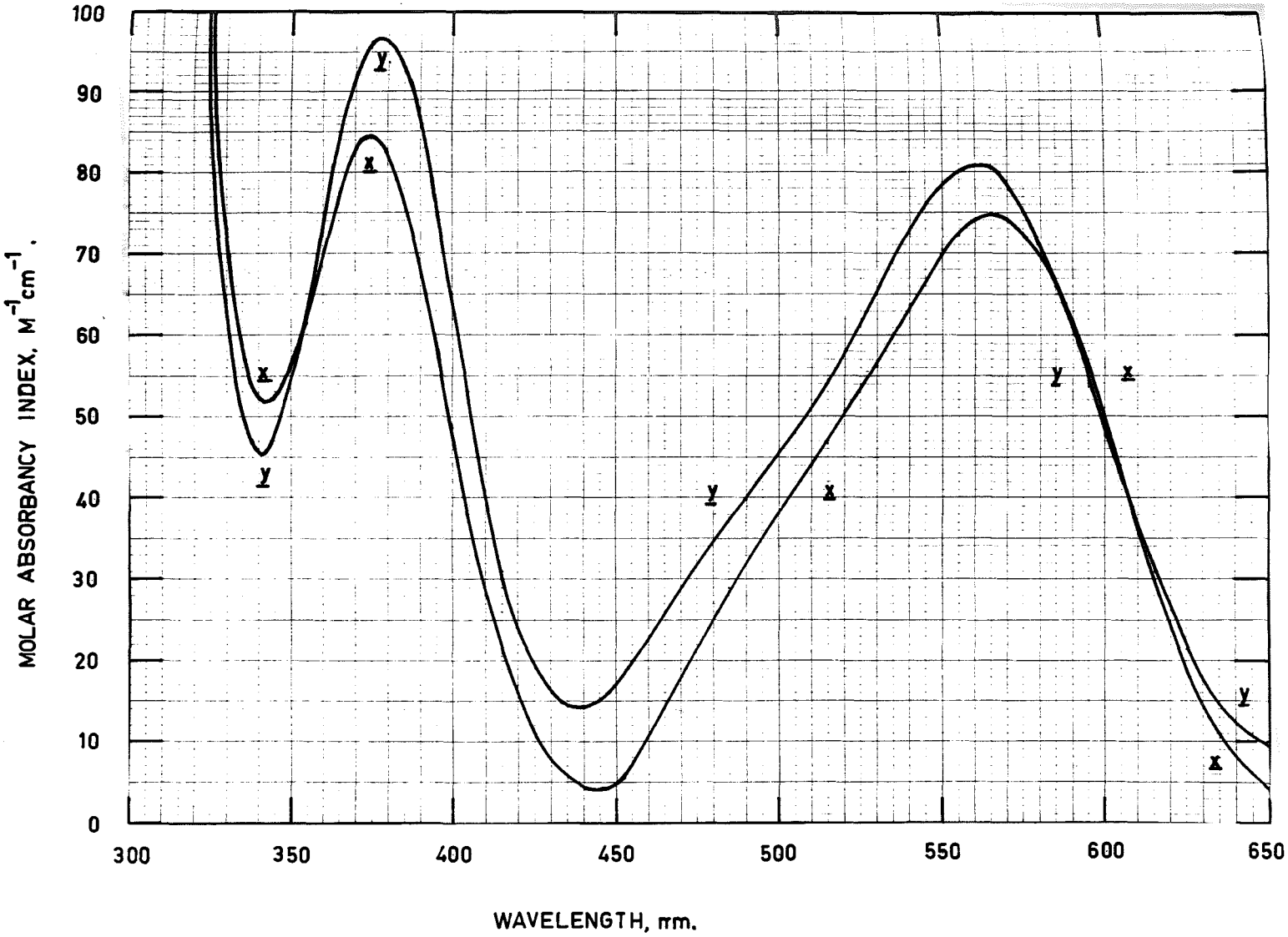


Figure 3.27 Visible absorption spectra of x and y - $Co(ibn)(dpt)Cl^{2+}$ in 0.1 F $HClO_4$ at 20-25°.

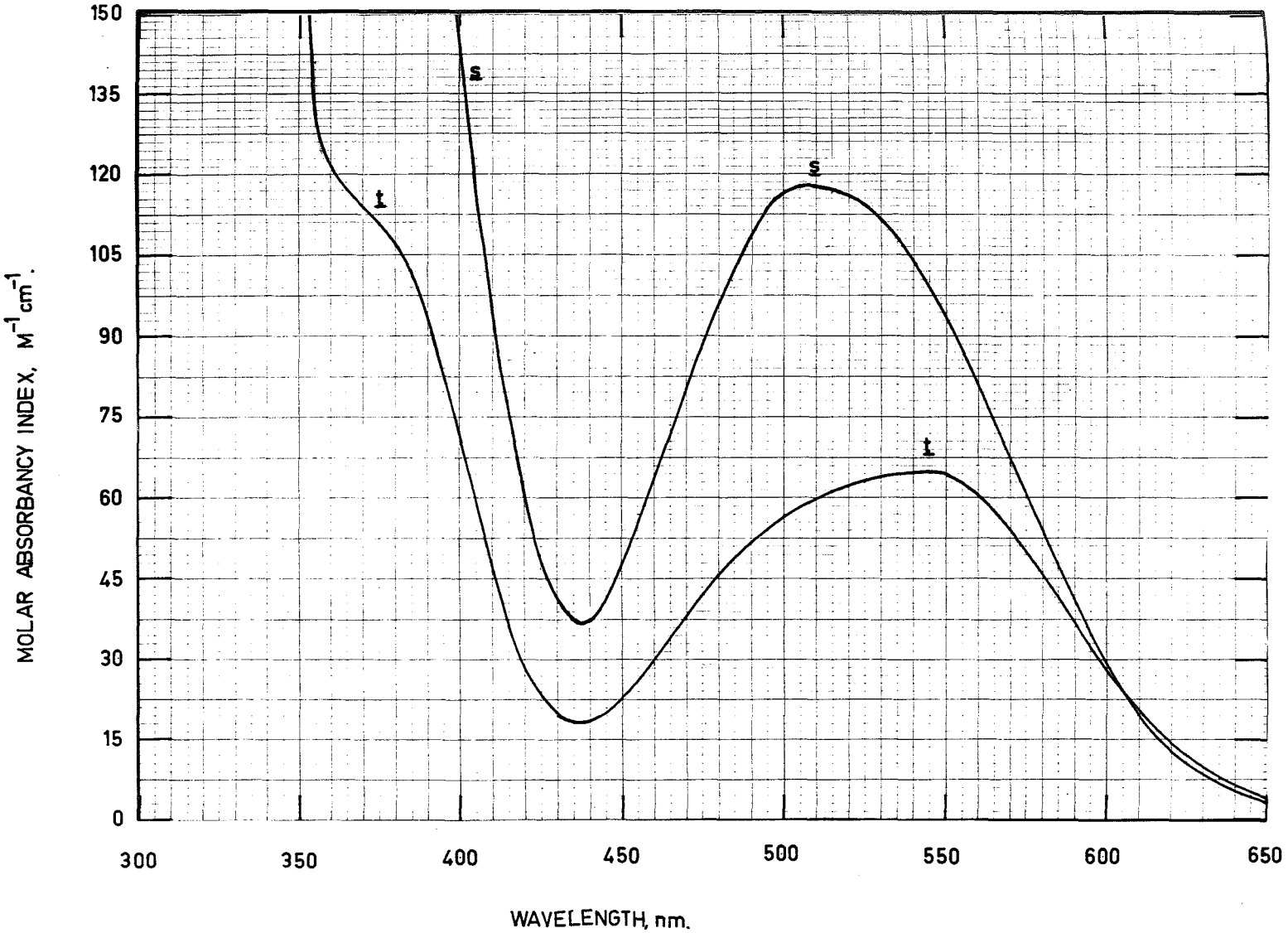


Figure 3.28 Visible absorption spectra of s and t - $Co(stien)(dpt)Cl^{2+}$ in 0.1 F $HClO_4$ at 20-25°.

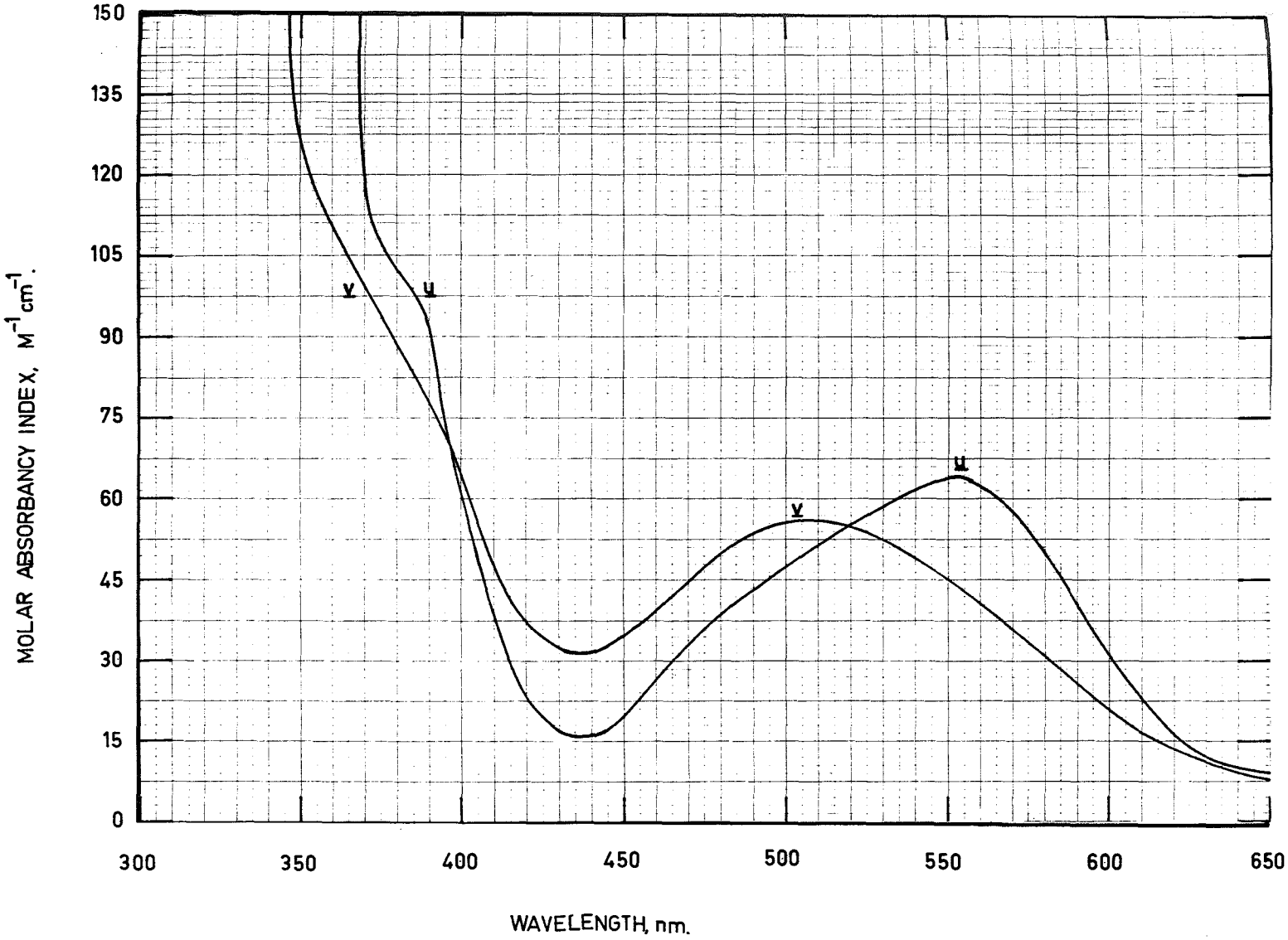


Figure 3.29 Visible absorption spectra of u and v - $Co(stien)(dpt)Cl^{2+}$ in 0.1 F $HClO_4$ at 20-25°.

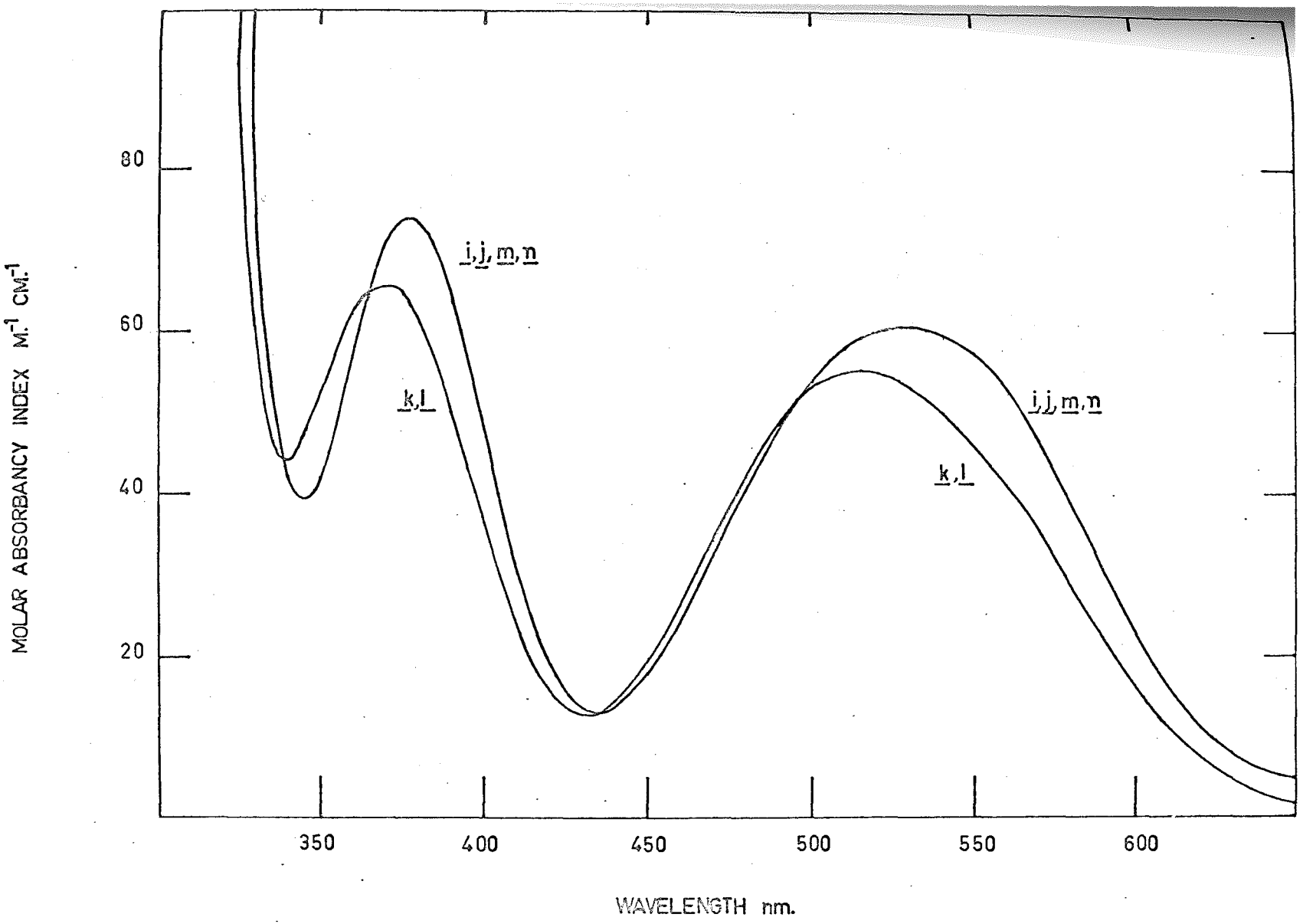


Figure 3.30 Visible absorption spectra of i, j, k, l, m and n - $Co(tmd)(dpt)Cl^{2+}$ in 0.1 F $HClO_4$ at 20-25°.

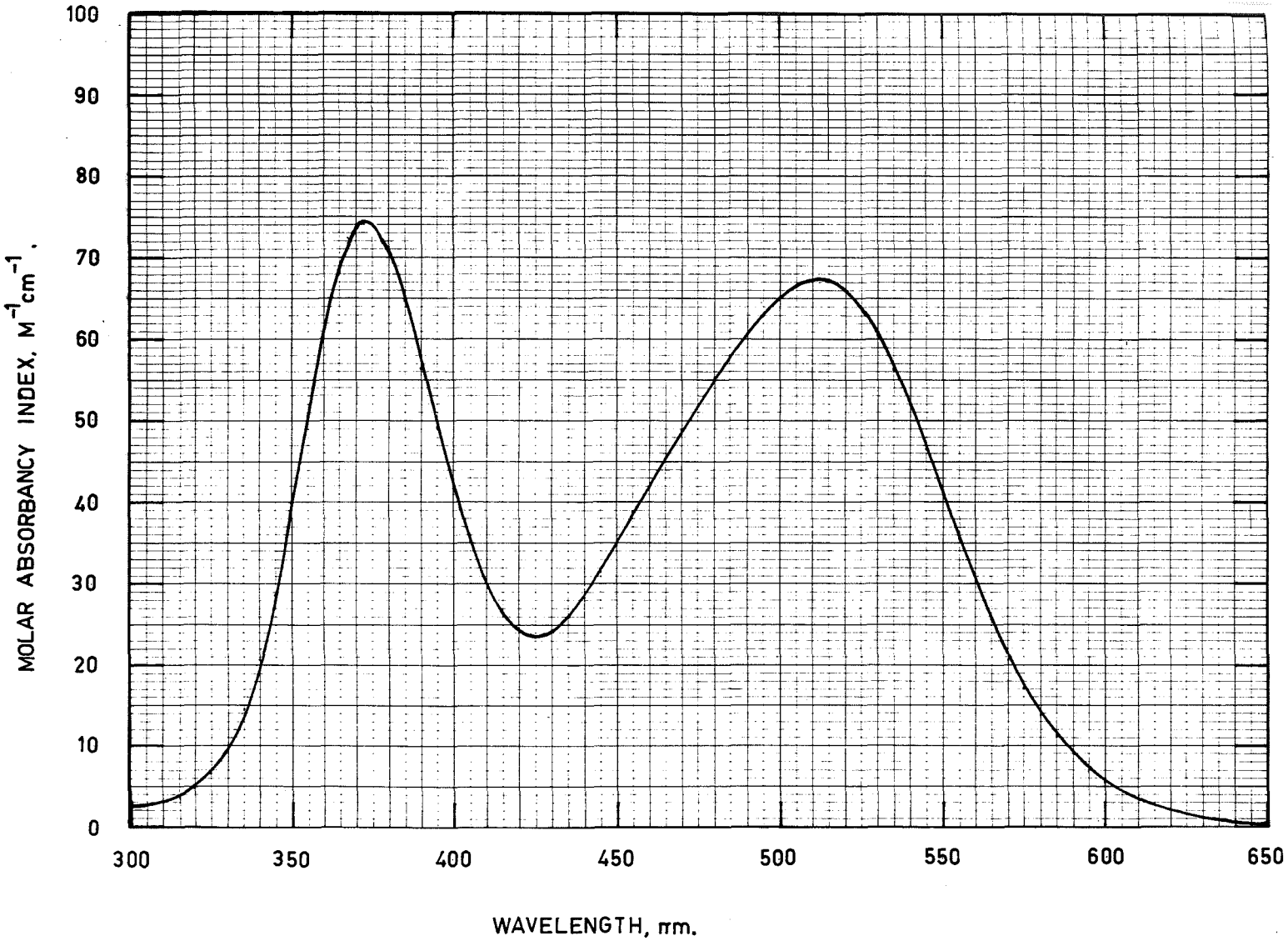


Figure 3.44 Visible absorption spectrum of π - $Cr(en)(dien)Cl^{2+}$ in 0.1 F $HClO_4$ at 20-25°.

Table 3.1

Visible Absorption Maxima and Minima for $Co(AA)(ABA)X^{n+}$, (AA = Bidentate linear polyamine, ABA = tridentate linear polyamine) π-$Cr(en)(dien)Cl^{2+}$, α- and β-$M(tetren)X^{n+}$ and $M(NH_3)_5X^{n+}$ (M = CoCr) in Aqueous Solution at 20-25°. [1]

Complex	λmin	λmax	λmin	λmax	λmin	λmax
ω-$Co(en)(dien)Cl^{2+}$	323 (75.0)	358 (100.8)	416 (19.3)	480sh [3] (60.0)		532 (92.0)
π-$Co(en)(dien)Cl^{2+}$	326 (33.6)	361 (71.0)	412 (15.0)	475sh (44.0)		525 (67.0)
κ-$Co(en)(dien)Cl^{2+}$	332 (35.2)	366 (87.9)	416 (30.3)	488sh (84.0)		515 (85.6)
α-$Co(tetren)Cl^{2+}$ [4]	328 (43.6)	362 (103)	417 (37.5)	480sh (105)		522 (109)
β-$Co(tetren)Cl^{2+}$ [4]	332 (64.5)	360 (107)	415 (37.2)	480 (101)	508 (97.3)	525 (98.6)
$Co(NH_3)_5Cl^{2+}$ [5]		364 (46.8)		467sh (11.0)		534 (50.1)
ω-$Co(en)(dien)Br^{2+}$			419 (22.2)	462sh (46.0)		538 (99.8)
π-$Co(en)(dien)Br^{2+}$			419 (20.2)	461sh (35.1)		537 (69.6)
κ-$Co(en)(dien)Br^{2+}$			420 (42.2)	476sh (84.4)		535 (97.0)
α-$Co(tetren)Br^{2+}$ [4]			423 (48.1)	480sh (100)		548 (132)
β-$Co(tetren)Br^{2+}$ [4]			422 (46.5)	480 (98.0)	495 (97.8)	550 (121)
$Co(NH_3)_5Br^{2+}$ [5]		310sh (831)		470sh (11.5)		552 (57.6)
ω-$Co(en)(dien)I^{2+}$	332 (1400)	374 (3500)	497 (69.3)			574 (164)
κ-$Co(en)(dien)I^{2+}$	333 (1800)	378 (4800)	510 (240)			567 (297)
$Co(NH_3)_5I^{2+}$ [6]		383 (269)	527 (56)			581 (79.5)

Complex	λ min	λmax	λ min	λmax	λmin	λ max
ω-Co(en)(dien)N_3^{2+}	266 (2590)	304 (7260)	432 (72.8)			507 (338)
π-Co(en)(dien)N_3^{2+}	262 (1790)	303 (8270)	431 (99.5)			506 (452)
K-Co(en)(dien)N_3^{2+}	262 (1740)	303 (7770)	431 (97.2)			504 (450)
α-Co(tetren)N_3^{2+} 4			432 (117)			508 (490)
$Co(NH_3)_5N_3^{2+}$ 7						519 (257)
ω-Co(en)(dien)NO_2^{2+}	290 (792)	325 (1750)	394 (40.5)			452 (139)
π-Co(en)(dien)NO_2^{2+}	288 (659)	322 (1340)	387 (29.4)			445 (109)
K-Co(en)(dien)NO_2^{2+}	292 (738)	326 (1440)	393 (38.3)			456 (157)
β-Co(tetren)NO_2^{2+} 4			397 (51.6)			460 (207)
$Co(NH_3)_5NO_2^{2+}$ 8		325 (1700)				458 (219)
$Co(NH_3)_5NO_2^{2+}$ 7		325 (1660)				458 (100)
ω-Co(en)(dien)NCS^{2+}	271 (997)	303 (1590)	409 (46.8)			482 (237)
π-Co(en)(dien)NCS^{2+}	275 (1040)	303 (1460)	413 (42.0)			486 (199)
K-Co(en)(dien)NCS^{2+}	273 (1140)	304 (1700)	409 (61.1)			482 (269)
α-Co(tetren)NCS^{2+} 4			415 (50.8)			490 (219)
β-Co(tetren)NCS^{2+} 4			412 (71.7)			487 (318)
$Co(NH_3)_5NCS^{2+}$ 7,9		357sh (398)	430 (35.5)			497 (186)
π-Co(en)(dien)O_2CH^{2+}	300 (253)	352 (304)	396 (11.4)			456 (32.3)
K-Co(en)(dien)O_2CH^{2+}	309 (24.8)	352 (84.4)	400 (11.2)			484 (112)

Complex	λmin	λmax	λmin	λmax	λmin	λmax
$Co(NH_3)_5O_2CH^{2+}$ 10		352 (44.7)				503 (58.9)
π-$Co(en)(dien)O_2CCH_3^{2+}$	301 (242)	352 (382)	397 (13.8)			458 (41.3)
κ- $Co(en)(dien)O_2CCH_3^{2+}$	309 (226)	352 (102.5)	401 (15.5)			486 (135)
$Co(NH_3)_5O_2CCH_3^{2+}$ 10		352 (50.1)				504 (66.1)
κ-$Co(en)(dien)O_2C(CH_2)_2Ph^{2+}$		349sh (229)	403 (45.5)			488 (170)
κ-$Co(en)(dien)O_2C(CHOH)CH_3^{2+}$		334sh (132)	397 (12.6)			488 (170)
κ-$Co(en)(dien)O_2CPh^{2+}$	318 (49.0)	351 (102)	403 (19.4)			487 (127)
ω-$Co(en)(dien)OH^{2+}$	308 (32.6)	357 (96.9)		368sh (94.7)	420 (29.4)	495 (94.7)
π-$Co(en)(dien)OH^{2+}$	312 (27.9)	358 (83.2)		369sh (79.6)	420 (19.4)	492 (97.6)
κ-$Co(en)(dien)OH^{2+}$	311 (38.8)	351 (96.1)		363sh (93.0)	416 (35.7)	487 (111)
α-$Co(tetren)OH^{2+}$ 4		348 (83.2)			417 (51)	490 (149)
$Co(NH_3)_5OH^{2+}$ 11	360 (69)	370 (70.8)			425 (20)	503 (62.5)
ω-$Co(en)(dien)OH_2^{3+}$	300 (30.3)	342 (86.2)	398 (17.0)			487 (72.1)
π-$Co(en)(dien)OH_2^{3+}$	303 (20.5)	346 (71.0)	397 (21.0)			476 (78.5)
κ-$Co(en)(dien)OH_2^{3+}$	304 (22.2)	361 (80.2)	402 (27.4)			473 (99.5)
α-$Co(tetren)OH_2^{3+}$ 4		350 (85.3)	405 (33.0)			472 (122)
$Co(NH_3)_5OH_2^{3+}$ 12		340				485 (48)
π-$Co(en)(dien)NO_3^{2+}$	322 (146)	345 (154)	400 (88.9)			467 (146)
$Co(NH_3)_5NO_3^{2+}$ 9		353 (40.0)				500 (57.3)

Complex	λmin	λmax	λmin	λmax	λmin	λmax
π-Cr(en)(dien)Cl^{2+}	293 (2.1)	373 (74.3)	425 (23.8)	455sh (38.0)		512 (67.5)
α-Cr(tetren)Cl^{2+} 4		375 (82.0)	422 (45.4)			495 (118)
Cr(NH$_3$)$_5$Cl^{2+} 13		375 (39)				512 (36)
Cr(NH$_3$)$_5$Cl^{2+} 6		376 (43.7)	452 (7.9)			515 (38)
Cr(NH$_3$)$_5$Cl^{2+} 14		375 (33.9)				511 (34.6)
H-Co(pn)(dien)Cl^{2+}	326 (60.6)	358 (100.9)	417 (17.6)	477sh (56.4)		532 (94.2)
I-Co(pn)(dien)Cl^{2+}	328 (36.8)	361 (78.1)	415 (15.9)	462sh (39.7)		528 (75.9)
A-Co(pn)(dien)Cl^{2+}	327 (32.9)	368 (84.2)	417 (27.7)	483sh (82.0)		518 (83.9)
D-Co(pn)(dien)Cl^{2+}	328 (38.8)	359 (74.4)	413 (15.0)	450sh (33.6)		525 (70.1)
B-Co(pn)(dien)Cl^{2+}	328 (33.9)	367 (85.6)	417 (29.3)	478sh (83.7)		517 (86.1)
G-Co(pn)(dien)Cl^{2+}	332 (102)	352 (107)	413 (30.2)	479 (81.9)		527sh (73.4)
C-Co(pn)(dien)Cl^{2+}		327sh (267)	407 (22.3)	465sh (48.9)		525 (58.0)
"E"-Co(pn)(dien)X^{2+}	304 (910)	325 (990)	402 (39.4)	462 (107)		542sh (39.1)
Synthetic "E" 15	304 (925)	325 (963)	402 (39.1)	462 (112)		542sh (38.3)
"F"-Co(pn)(dien)X^{2+}	299 (681)	326 (958)	400 (38.5)	461 (115)		545sh (26.7)
Synthetic "F" 16	299 (702)	326 (1028)	400 (32.3)	461 (114)		545sh (30.8)
H-Co(pn)(dien)Br^{2+}		378sh (106)	426 (19.3)	468sh (43.1)		546 (113)
I-Co(pn)(dien)Br^{2+}		376sh (103)	423 (17.9)	463sh (34.2)		541 (71.7)

Complex	λmin	λmax	λmin	λmax	λmin	λmax
A-Co(pn)(dien)Br^{2+}		378sh (118)	425 (36.4)	473sh (76.3)		541 (92.6)
D-Co(pn)(dien)Br^{2+}		378sh (93.7)	422 (18.3)	463sh (35.1)		539 (73.7)
B-Co(pn)(dien)Br^{2+}		375sh (123)	424 (35.9)	474sh (76.7)		538 (90.4)
G-Co(pn)(dien)Br^{2+}		385sh (95.3)	424 (36.3)	490sh (78.2)		539 (86.9)
H-Co(pn)(dien)I^{2+}			503 (82.2)			576 (165)
G-Co(pn)(dien)I^{2+}	335 (756)		518 (87.9)			563 (101)
H-Co(pn)(dien)N_3^{2+}	262 (1375)	305 (8170)	432 (74.6)			506 (403)
A-Co(pn)(dien)N_3^{2+}	262 (1815)	304 (8305)	432 (81.3)			505 (436)
G-Co(pn)(dien)N_3^{2+}	263 (2330)	304 (8130)	432 (72.2)			507 (396)
H-Co(pn)(dien)NO_2^{2+}	289 (766)	325 (1735)	393 (33.8)			452 (127)
I-Co(pn)(dien)NO_2^{2+}	289 (766)	324 (1865)	392 (35.7)			451 (121)
A-Co(pn)(dien)NO_2^{2+}	290 (804)	324 (1655)	392 (37.9)			450 (172)
D-Co(pn)(dien)NO_2^{2+}	290 (711)	325 (1490)	393 (28.4)			450 (119)
B-Co(pn)(dien)NO_2^{2+}	293 (609)	327 (1175)	394 (26.4)			457 (128)
G-Co(pn)(dien)NO_2^{2+}	292 (774)	326 (1525)	394 (39.1)			455 (151)
C-Co(pn)(dien)NO_2^{2+}	295 (690)	321 (946)	392 (29.6)			448 (82.5)
H-Co(pn)(dien)NCS^{2+}	271 (945)	306 (1630)	414 (47.6)			494 (253)
A-Co(pn)(dien)NCS^{2+}	287 (696)	304 (750)	410 (25.1)			487 (174)
D-Co(pn)(dien)NCS^{2+}	274 (1110)	304 (1570)	414 (44.3)			489 (203)

Complex	λmin	λmax	λmin	λmax	λmin	λmax
B-Co(pn)(dien)NCS^{2+}	274 (1095)	306 (1660)	412 (56.1)			488 (264)
G-Co(pn)(dien)NCS^{2+}	277 (1245)	307 (1710)	411 (56.6)			486 (225)
U-Co(ibn)(dien)Cl^{2+}	328 (51.5)	358 (74.1)	414 (24.0)	475sh (54.6)		536 (66.5)
V-Co(ibn)(dien)Cl^{2+}	329 (44.1)	364 (102)	421 (19.6)	470sh (54.6)		538 (111)
O-Co(ibn)(dien)Cl^{2+}	332 (42.0)	367 (90.0)	418 (31.8)	489 (94.6)		530sh (84.4)
Q-Co(ibn)(dien)Cl^{2+}	330 (37.5)	372 (93.5)	422 (32.1)	475sh (89.8)		508 (97.2)
P-Co(ibn)(dien)Cl^{2+}	329 (34.1)	371 (92.2)	421 (30.8)	485sh (94.3)		505 (98.3)
R-Co(ibn)(dien)Cl^{2+}	332 (39.3)	372 (91.1)	422 (32.1)	485sh (89.3)		508 (90.9)
W-Co(ibn)(dien)Cl^{2+}	323 (62.7)	346 (72.6)	412 (41.3)	475 (97.2)		560sh (41.7)
"S"-Co(ibn)(dien)X^{2+}	312 (475)	326 (500)	410 (42.8)	472 (107)		538sh (61.8)
Synthetic "S" [17]	312 (427)	326 (470)	410 (39.5)	472 (105)		538sh (69.4)
"T"-Co(ibn)(dien)X^{2+}		327sh (266)	416 (52.4)	480 (112)		537sh (87.8)
Synthetic "T" [18]		327sh (229)	416 (47.7)	480 (98.0)		537sh (88.5)
Q-Co(ibn)(dien)Br^{2+}		382sh (132)	431 (38.3)	495sh (81.9)		548 (98.9)
R-Co(ibn)(dien)Br^{2+}		376sh (145)	432 (37.0)	499sh (81.7)		550 (96.9)
U-Co(ibn)(dien)NO_2^{2+}	292 (802)	327 (1635)	396 (38.2)			452 (153)
V-Co(ibn)(dien)NO_2^{2+}	291 (783)	326 (1790)	396 (39.1)			451 (148)
O-Co(ibn)(dien)NO_2^{2+}	294 (826)	328 (1615)	399 (41.0)			457 (157)

Table 3.1(contd.) 7

Complex	λmin	λmax	λmin	λmax	λmin	λmax
Q-Co(ibn)(dien)NO_2^{2+}	294 (784)	328 (1520)	397 (36.1)			460 (164)
P-Co(ibn)(dien)NO_2^{2+}	294 (707)	328 (1425)	399 (34.3)			457 (133)
R-Co(ibn)(dien)NO_2^{2+}	293 (746)	328 (1515)	398 (31.9)			458 (137)
W-Co(ibn)(dien)NO_2^{2+}	294 (507)	328 (1030)	398 (28.4)			460 (123)
XI-Co(Nip-ibn)(dien)Cl^{2+}	342 (53.8)	375 (93.4)	429 (20.9)	495sh (65.1)		546 (89.3)
XIII-Co(Nip-ibn)(dien)Cl^{2+}		355sh (124)	424 (18.7)	475sh (51.7)		544 (75.5)
XV-Co(Nip-ibn)(dien)Cl^{2+}	342 (55.5)	373 (87.9)	427 (17.6)	480sh (53.3)		544 (84.0)
X-Co(Nip-ibn)(dien)Cl^{2+}	340 (38.3)	381 (102)	434 (26.7)	510 (99.0)		545sh (86.8)
XII-Co(Nip-ibn)(dien)Cl^{2+}	342 (53.8)	372 (85.5)	426 (18.8)	480sh (62.4)		533 (82.7)
XIV-Co(Nip-ibn)(dien)Cl^{2+}	310 (974)	324 (1015)	401 (35.5)	462 (111)		
o-Co(stien)(dien)Cl^{2+}	350 (128)	365 (135)	426 (21.3)	470sh (53.8)		534 (106)
p-Co(stien)(dien)Cl^{2+}		360sh (95.2)	418 (21.5)	470sh (44.4)		528 (70.1)
q-Co(stien)(dien)Cl^{2+}		370sh (126)	427 (38.8)	493 (85.2)		520pl[19] (83.1)
r-Co(stien)(dien)Cl^{2+}		375sh (111)	425 (33.8)	475sh (70.9)		530 (84.4)
o-Co(stien)(dien)Br^{2+}		380sh (217)	432 (35.0)	485sh (82.6)		546 (163)
p-Co(stien)(dien)Br^{2+}		383sh (128)	428 (29.5)	464sh (44.1)		534 (69.0)
p-Co(stien)(dien)NO_2^{2+}		319sh (471)	404 (94.0)			442 (115)

Complex	λmin	λmax	λmin	λmax	λmin	λmax
h-Co(tmd)(dien)Cl^{2+}	327 (40.7)	364 (98.5)	424 (19.0)	465sh (40.0)		546 (96.6)
d-Co(tmd)(dien)Cl^{2+}	329 (39.3)	369 (97.0)	424 (26.0)	470sh (55.7)		535 (75.1)
e-Co(tmd)(dien)Cl^{2+}	329 (39.3)	369 (97.0)	424 (26.1)	475sh (58.2)		535 (75.0)
f-Co(tmd)(dien)Cl^{2+}	330 (38.8)	369 (96.8)	424 (26.0)	473sh (56.9)		535 (74.8)
a-Co(tmd)(dien)Cl^{2+}	333 (44.1)	372 (78.4)	421 (31.8)	487 (84.6)		540sh (62.7)
b-Co(tmd)(dien)Cl^{2+}	335 (44.4)	369 (79.0)	421 (32.1)	487 (84.7)		540sh (613)
c-Co(tmd)(dien)Cl^{2+}	328 (45.2)	368 (90.9)	417 (36.6)	491 (91.9)		522sh (88.6)
"g"-Co(tmd)(dien)X^{2+}	317 (354)	326 (359)	415 (39.0)	468 (73.6)	520 (59.6)	528 (65.0)
Synthetic "g" [20]	317 (351)	326 (362)	415 (39.2)	468 (73.4)	520 (60.1)	528 (66.3)
h-Co(tmd)(dien)Br^{2+}		391sh (77.5)	434 (12.6)	476sh (28.9)		563 (124)
d-Co(tmd)(dien)Br^{2+}		390sh (91.6)	432 (22.6)	483sh (47.2)		552 (70.8)
a-Co(tmd)(dien)Br^{2+}		386sh (102)	431 (26.3)	481sh (49.7)		555 (77.0)
d-Co(tmd)(dien)N_3^{2+}	271 (3115)	311 (7495)	438 (66.8)			513 (298)
h-Co(tmd)(dien)NO_2^{2+}	294 (770)	329 (1685)	399 (38.4)			457 (151)
f-Co(tmd)(dien)NO_2^{2+}	295 (705)	327 (1245)	397 (39.2)			458 (134)
f-Co(tmd)(dien)NO_2^{2+} [21]	295 (700)	327 (1250)	397 (40.1)			459 (136)
f-Co(tmd)(dien)NO_2^{2+} [22]	295 (710)	327 (1245)	396 (39.4)			458 (136)
b-Co(tmd)(dien)NO_2^{2+} [23]	297 (770)	329 (1400)	399 (38.2)			462 (137)
b-Co(tmd)(dien)NO_2^{2+}	296 (775)	329 (1410)	399 (38.3)			462 (138)

Complex	λmin	λmax	λmin	λmax	λmin	λmax
c-Co(tmd)(dien)NO_2^{2+}	293 (1190)	327 (2250)	395 (82.1)			454 (246)
IV-Co(Me-tmd)(dien)Cl^{2+}	347 (89.5)	369 (93.6)	433 (28.5)	490sh (54.9)		544 (62.5)
V-Co(Me-tmd)(dien)Cl^{2+}	337 (30.7)	379 (104)	434 (16.8)	505sh (68.2)		546 (80.2)
I-Co(Me-tmd)(dien)Cl^{2+}	317 (670)	327 (681)	420 (37.5)	479 (85.3)		520sh (60.1)
II-Co(Me-tmd)(dien)Cl^{2+}		380sh (107)	427 (31.6)	495 (89.6)		550sh (58.1)
III-Co(Me-tmd)(dien)Cl^{2+}	340 (59.2)	378 (98.8)	430 (31.1)	500 (93.7)		550sh (65.6)
V-Co(Me-tmd)(dien)Br^{2+}		393sh (112)	442 (25.7)	497sh (62.5)		560 (78.6)
III-Co(Me-tmd)(dien)Br^{2+}		392sh (106)	439 (25.0)	497sh (55.1)		556 (72.3)
V-Co(Me-tmd)(dien)N_3^{2+}	279 (3985)	311 (7115)	452 (61.0)			526 (292)
I-Co(Me-tmd)(dien)NO_2^{2+}	301 (866)	331 (1370)	406 (30.7)			465 (125)
V-Co(Me-tmd)(dien)OH^{2+}	322 (68.5)	352 (103)	435 (32.1)			508 (101)
VII-Co(Bu-tmd)(dien)Cl^{2+}	346 (72.6)	377 (100)	435 (26.5)	485sh (60.6)		545 (73.6)
VI-Co(Bu-tmd)(dien)Cl^{2+}	355 (108)	367 (109)	429 (27.8)	498 (95.1)		545sh (63.7)
VII-Co(Bu-tmd)(dien)Br^{2+}		382sh (114)	431 (33.9)	494 (92.3)		543sh (57.6)
VI- Co(Bu-tmd)(dien)NO_2^{2+}	309 (885)	330 (1095)	407 (31.9)			470 (111)
VIII-Co(tmd-hex)(dien)Cl^{2+}	343 (32.1)	373 (51.0)	428 (16.5)	480sh (20.4)		532 (28.9)

Complex	λmin	λmax	λmin	λmax	λmin	λmax
IX-Co(tmd-hex)(dien)Cl^{2+}	353 (76.2)	382 (121)	440 (19.8)	495sh (65.1)		550 (88.3)
1-Co(1,4-bn)(dien)Cl^{2+}	334 (38.0)	371 (85.3)	426 (17.6)	481sh (58.4)		523 (72.4)
Σ-Co(2,3-tri)(en)Cl^{2+}	331 (37.0)	363 (73.9)	418 (16.1)	465sh (40.9)		534 (65.0)
η-Co(2,3-tri)(en)Cl^{2+}	329 (28.7)	367 (80.7)	422 (16.7)	465sh (42.1)		540 (72.5)
"ρ"-Co(2,3-tri)(en)X^{2+}	322 (182)	329 (183)	417 (21.5)	482 (55.2)	496 (54.3)	540 (63.5)
Synthetic "ρ" 24	322 (174)	329 (199)	417 (21.9)	482 (55.3)	496 (54.6)	540 (65.1)
"ι"-Co(2,3-tri)(en)X^{2+}	308 (483)	325 (537)	405 (27.0)	463 (70.7)		535sh (43.2)
Synthetic "ι" 25	308 (478)	325 (529)	405 (23.7)	463 (67.1)		535sh (44.3)
"Δ"-Co(2,3-tri)(en)X^{2+}	299 (645)	327 (987)	400 (31.3)	456 (96.6)		550sh (21.4)
Synthetic "Δ" 26	299 (651)	327 (983)	400 (31.4)	456 (94.4)		550sh (19.9)
Σ-Co(2,3-tri)(en)Br^{2+}		365sh (177)	430 (20.4)	473sh (38.0)		554 (75.5)
η-Co(2,3-tri)(en)Br^{2+}		366sh (167)	432 (22.0)	477sh (40.1)		556 (80.7)
η-Co(2,3-tri)(en)I^{2+}	338 (970)	380 (2230)	518 (47.5)			591 (119)
Σ-Co(2,3-tri)(en)NO_2^{2+}	294 (698)	328 (1375)	397 (32.3)			455 (117)
η-Co(2,3-tri)(en)NO_2^{2+}	294 (606)	327 (1155)	400 (29.1)			456 (96.9)
J-Co(pn)(dpt)Cl^{2+}	342 (42.3)	375 (69.1)	433 (15.7)	482sh (42.2)		541 (58.9)

Complex	λmin	λmax	λ min	λmax	λ min	λ max
L-Co(pn)(dpt)Cl^{2+}	339 (40.2)	376 (88.0)	432 (15.7)	482sh (47.2)		545 (73.9)
K-Co(pn)(dpt)Cl^{2+}	340 (58.7)	375 (94.2)	434 (17.2)	477sh (44.0)		553 (74.4)
M-Co(pn)(dpt)Cl^{2+}	339 (34.3)	380 (94.0)	437 (16.3)	493sh (49.5)		557 (77.8)
α-Co(en)(dpt)Cl^{2+} 27	337 (30.8)	374 (90.1)	431 (13.0)	517sh (60.1)		542 (75.1)
α-Co(en)(dpt)Cl^{2+} 28		374 (86.9)	430 (15.8)			542 (73.5)
β-Co(en)(dpt)Cl^{2+} 27	335 (31.5)	375 (83.0)	432 (13.8)	520sh (62.0)		542 (70.1)
β-Co(en)(dpt)Cl^{2+} 28		379 (95.3)	437 (15.2)			553 (78.1)
J-Co(pn)(dpt)Br^{2+}		400sh (88.7)	445 (24.8)	497sh (50.9)		568 (74.0)
L-Co(pn)(dpt)Br^{2+}		375sh (180)	439 (23.0)	489sh (55.9)		559 (90.8)
K-Co(pn)(dpt)Br^{2+}		393sh (91.1)	443 (20.5)	497sh (49.8)		566 (74.2)
M-Co(pn)(dpt)Br^{2+}		395sh (92.5)	444 (23.4)	494sh (49.1)		565 (75.0)
α-Co(en)(dpt)Br^{2+} 27			447 (20.4)	486sh (42.9)		551 (66.9)
β-Co(en)(dpt)Br^{2+} 27			437 (10)	532sh (51)		564 (63)
J-Co(pn)(dpt)NO_2^{2+}	302 (1120)	334 (2260)	407 (31.3)			471 (135)
L-Co(pn)(dpt)NO_2^{2+}	301 (844)	332 (1500)	405 (31.6)			468 (128)
K-Co(pn)(dpt)NO_2^{2+}	301 (725)	333 (1205)	407 (32.7)			468 (114)
M-Co(pn)(dpt)NO_2^{2+}	302 (891)	334 (1535)	406 (34.2)			470 (145)
α-Co(en)(dpt)NO_2^{2+} 27			403 (53.8)			462 (143)
β-Co(en)(dpt)NO_2^{2+} 27			405 (39.5)			468 (133)

Table 3.1(contd.) 12

Complex	λmin	λmax	λmin	λmax	λmin	λmax
w-Co(ibn)(dpt)Cl^{2+}	342 (45.0)	373 79.9)	436 (9.4)	480sh (30.9)		550 (73.8)
z-Co(ibn)(dpt)Cl^{2+}	343 (51.5)	373 (82.5)	433 (16.2)	470sh (31.5)		558 (70.6)
x-Co(ibn)(dpt)Cl^{2+}	342 (51.5)	375 (84.3)	444 (3.7)	495sh (35.6)		565 (75.0)
y-Co(ibn)(dpt)Cl^{2+}	341 (45.3)	378 (96.6)	438 (14.1)	485sh (37.8)		562 (81.1)
s-Co(stien)(dpt)Cl^{2+}		410sh (75.9)	436 (24.0)	508 (118)		545sh (100)
t-Co(stien)(dpt)Cl^{2+}		375sh (111)	436 (18.4)	495sh (54.0)		545 (64.8)
u-Co(stien)(dpt)Cl^{2+}		385sh (93.4)	437 (15.9)	490sh (43.6)		553 (64.4)
v-Co(stien)(dpt)Cl^{2+}		370sh (104)	437 (31.0)	503 (56.1)		545sh (47.3)
i-Co(tmd)(dpt)Cl^{2+}	343 (39.3)	377 (73.8)	435 (13.0)	527 (60.4)		555sh (55.2)
j-Co(tmd)(dpt)Cl^{2+}	344 (38.9)	377 (74.0)	434 (12.6)	527 (60.4)		555sh (55.1)
m-Co(tmd)(dpt)Cl^{2+}	344 (39.4)	377 (74.0)	435 (12.8)	528 (60.5)		555sh (55.2)
n-Co(tmd)(dpt)Cl^{2+}	344 (39.5)	377 (74.1)	435 (13.1)	527 (60.4)		555sh (55.4)
k-Co(tmd)(dpt)Cl^{2+}	340 (44.2)	372 (65.3)	432 (12.7)	514 (55.2)		565sh (38.5)
l-Co(tmd)(dpt)Cl^{2+}	340 (44.1)	372 (65.4)	432 (12.8)	514 (55.3)		565sh (38.3)
i-Co(tmd)(dpt)Br^{2+}		405sh (66.5)	444 (15.7)	492sh (44.7)		540br[29] (54.8)
n-Co(tmd)(dpt)Br^{2+}		405sh (66.9)	444 (15.8)	493sh (44.9)		541br (54.6)
k-Co(tmd)(dpt)Br^{2+}		386sh (93.4)	437 (20.3)	512sh (60.4)		553 (48.1)

Complex	λmin	λmax	λmin	λmax	λmin	λmax
i-Co(tmd)(dpt)N_3^{2+}			457 (66.4)			530 (274)
i-Co(tmd)(dpt)NO_2^{2+}	305 (1020)	334 (1590)	410 (26.8)			481 (120)
i-Co(tmd)(dpt)NO_2^{2+} 30	305 (1025)	334 (1580)	410 (26.5)			481 (121)
l-Co(tmd)(dpt)NO_2^{2+}	306 (1560)	336 (1655)	414 (46.4)			480 (188)
i-Co(tmd)(dpt)OH_2^{3+}		357sh (201)	430 (96.1)			515 (132)
i-Co(tmd)(dpt)OH^{2+}	332 (38.3)	367 (65.5)	442 (16.0)	516 (73.1)		550sh (49.4)

1 Everywhere, numbers inside parentheses are the molar absorbancy indices, a_M (extinction coefficients, ε) in $M^{-1}cm^{-1}$. Wavelengths are in nanometers (millimicrons), ±2 nm.

2 In 0.1 F $HClO_4$; in 0.1 F NaOH for the hydroxo cations.

3 sh = shoulder.

4 Data from references 12,13.

5 Data from reference 113.

6 Data from reference 114.

7 Data from reference 115.

8 Data from reference 116.

9 Data from reference 117.

10 Data from reference 118.

11 Data from reference 119.

12 Data from reference 120,121.

13 Data from reference 122.

14 Data from reference 123.

15 Calculated from 51% G-Co(pn)(dien)Cl^{2+} and 49% G-Co(pn)(dien)NO_2^{2+}.

16 Calculated from 44% A-Co(pn)(dien)Cl^{2+} and 56% A-Co(pn)(dien)NO_2^{2+}.

17 Calculated from 73% O-Co(ibn)(dien)Cl^{2+} and 27% O-Co(ibn)(dien)NO_2^{2+}.

18 Calculated from 71% P-Co(ibn)(dien)Cl^{2+} and 29% P-Co(ibn)(dien)NO_2^{2+}.

19 pl = plateaux.

20 Calculated from 73% f-Co(tmd)(dien)Cl^{2+} and 27% f-Co(tmd)(dien)NO_2^{2+}.

21 Derived from e-[Co(tmd)(dien)Cl]$ZnCl_4.H_2O$.

22 Derived from d-[Co(tmd)(dien)Cl]$ZnCl_4$.

23 Derived from a-[Co(tmd)(dien)Cl]$ZnCl_4$.

24 Calculated from 69% η-Co(2,3-tri)(en)Cl^{2+} and 31% η-Co(2,3-tri)(en)NO_2^{2+}.

25 Calculated from 63% Σ-Co(2,3-tri)(en)Cl^{2+} and 37% Σ-Co(2,3-tri)(en)NO_2^{2+}.

26 Calculated from 14% η-Co(2,3-tri)(en)Cl^{2+}, 14% Σ-Co(2,3-tri)(en)Cl^{2+} and 72% Σ-Co(2,3-tri)(en)NO_2^{2+}.

27 Data from reference 29,30.

28 Data from reference 37.

29 br = broad.

30 Derived from j-[Co(tmd)(dpt)Cl]$ZnCl_4.2H_2O$.

resolution is incomplete. The spectra obtained are all very similar to that obtained for (-)-β-Co(tetren)Cl^{2+}.[12,13]

(3) Crystallographic Space Groups

Unit cell dimensions and associated crystallographic space groups have been used as a method of characterising isomers and also for the detection of chloro-nitro crystallising mixtures ((5) Chapter 3).

All unit cell dimensions were calculated from precession photographs using Nickel filtered $CuK\bar{\alpha}$ X-irradiation ($\lambda CuK\bar{\alpha}$ = 1.5418Å). The data obtained for the seven isomers of $[Co(pn)(dien)Cl]ZnCl_4.xH_2O$ are presented in Table 3.2; for d (racemic) and e (racemic)-$[Co(tmd)(dien)Cl]ZnCl_4.xH_2O$ and V (racemic)-$[Co(Me\text{-}tmd)(dien)Cl]ZnCl_4$ in Table 3.3; and for $[Co(en)(ABA)X]ZnCl_4$ (ABA = dien, dpt, X = Cl^-, I^-, NO_2^-) in Table 3.4. Densities were determined by flotation in CCl_4-CH_3I.

(4) Nuclear Magnetic Resonance Spectra (NMR)

NMR spectra have been used as a method of characterisation of isomers, and also for the detection of chloro-nitro crystallising mixtures ((5) Chapter 3).

The NMR spectra of α, β and "γ"-$Co(en)(dpt)Cl^{2+}$ and α-$Co(en)(dpt)NO_2^{2+}$ (as the $ZnCl_4^{2-}$ salts) in d_6-DMSO are presented in Fig. 3.36. Similar spectra for ω, π, *K* and "ε"-$Co(en)(dien)Cl^{2+}$ and π-$Co(en)(dien)NO_2^{2+}$ are presented

Table 3.2

Crystallographic Data for the 7 $[Co(pn)(dien)Cl]ZnCl_4.xH_2O$ Isomers

Isomer	Crystal System	Space Group	Z	a(Å)	b(Å)	c(Å)	α	β	γ
A	Monoclinic	$P2_1/c$ (No.14)	4	9.40	10.87	18.51	-	107.2°	-
B	Monoclinic	Cc (No. 9)	4	9.63	13.17	13.90	-	93.6°	-
C	Triclinic	$P\bar{1}$ (No. 2)	2	8.65	12.44	7.02	96.6°	106.7°	98.9°
D	Monoclinic	P2 (No. 3)	2	7.89	10.57	10.68	-	99.0°	-
G	Monoclinic	C2/c (No.15)	8	15.47	10.76	21.28	-	96.5°	-
H	Orthorhombic	Pbca (No.61)	8	13.06	12.63	22.98	-	-	-
I	Triclinic	$P\bar{1}$ (No. 2)	2	6.91	13.52	10.22	99.3°	102.2°	90.6°

Table 3.3

Crystallographic Data for d-$[Co(tmd)(dien)Cl]ZnCl_4$, e-$[Co(tmd)(dien)Cl]ZnCl_4.H_2O$ and V-$[Co(Me\text{-}tmd)(dien)Cl]ZnCl_4$

Complex	Crystal System	Space Group	Z	a(Å)	b(Å)	c(Å)	β
d-$[Co(tmd)(dien)Cl]ZnCl_4$	Monoclinic	$P2_1/c$	4	10.23	9.64	16.67	96.5°
e-$[Co(tmd)(dien)Cl]ZnCl_4.H_2O$	Monoclinic	C2/c	8	9.73	11.42	28.91	91.0°
V-$[Co(Me\text{-}tmd)(dien)Cl]ZnCl_4$	Monoclinic	$P2_1$	2	10.45	8.30	10.45	94.3°

Table 3.4

Crystallographic Data for Some $[Co(en)(ABA)X]ZnCl_4$ Isomers [a]

ABA	Isomer[b]	X	Crystal System	Space Group	Z	a(Å)	b(Å)	c(Å)	β	Reference
dpt	α	NO_2	Orthorhombic	Pma2 or $Pma2_1$	2	8.73	6.74	15.35	-	This work
dpt	α	Cl	Hexagonal	$P6_3$	6	14.60	14.60	14.83	-	This work
dpt	γ	Cl	Hexagonal	$P6_3$	6	14.60	14.60	14.83	-	This work
dpt	α [c]	Cl	Orthorhombic	$Pma2$ or $Pma2_1$	4	12.52	7.26	14.84	-	This work
dpt	γ [c]	Cl	Orthorhombic	$Pma2$ or $Pma2_1$	4	12.52	7.24	14.76	-	This work
dpt	α [d]	Cl	Orthorhombic	$Pna2_1$	4	14.49(1)	9.123(6)	13.27(1)	-	32, 34
dpt	β	Cl	Monoclinic	$P2_1/c$	4	7.875(3)	15.824(11)	14.748(8)	94.69(5)°	32, 33
dien	π	NO_2	Monoclinic	$P2_1/n$	4	10.91	18.10	8.42	75° 10'	This work
dien	π	Cl	Monoclinic	$P2_1/n$	4	13.745(3)	8.202(2)	15.117(6)	98.557(14)°	This work
dien	ε	Cl	Monoclinic	$P2_1/n$	4	13.73	8.25	15.05	98° 35'	This work
dien		Cl	Monoclinic	Cc	4	9.676(1)	12.790(2)	13.888(3)	93.629(14)°	This work
dien		NO_2	Monoclinic	Cc	4	9.50	12.74	14.05	92.25°	This work
dien	ω	Cl	Orthorhombic	$Pna2_1$	4	14.86	7.85	14.32	-	25, 26
dien	ω [e]	Cl	Monoclinic	Cc	4	14.44	7.87	12.30	100.1°	25, 26
dien	ω [d]	I	Monoclinic	C2	4	14.80	8.53	13.06	99.4°	25, 26

[a] Errors in the unrefined cell dimensions are of the order of 0.25%, 71. Numbers in parentheses are estimated standard deviations in the least significant digits quoted and are derived from the inverse matrix in non-linear least-squares refined calculations. [b] Greek letters assigned as in Reference 30 and 72. [c] As the chloride salt. [d] As the iodide monohydrate salt. [e] as the chloride hemihydrate salt.

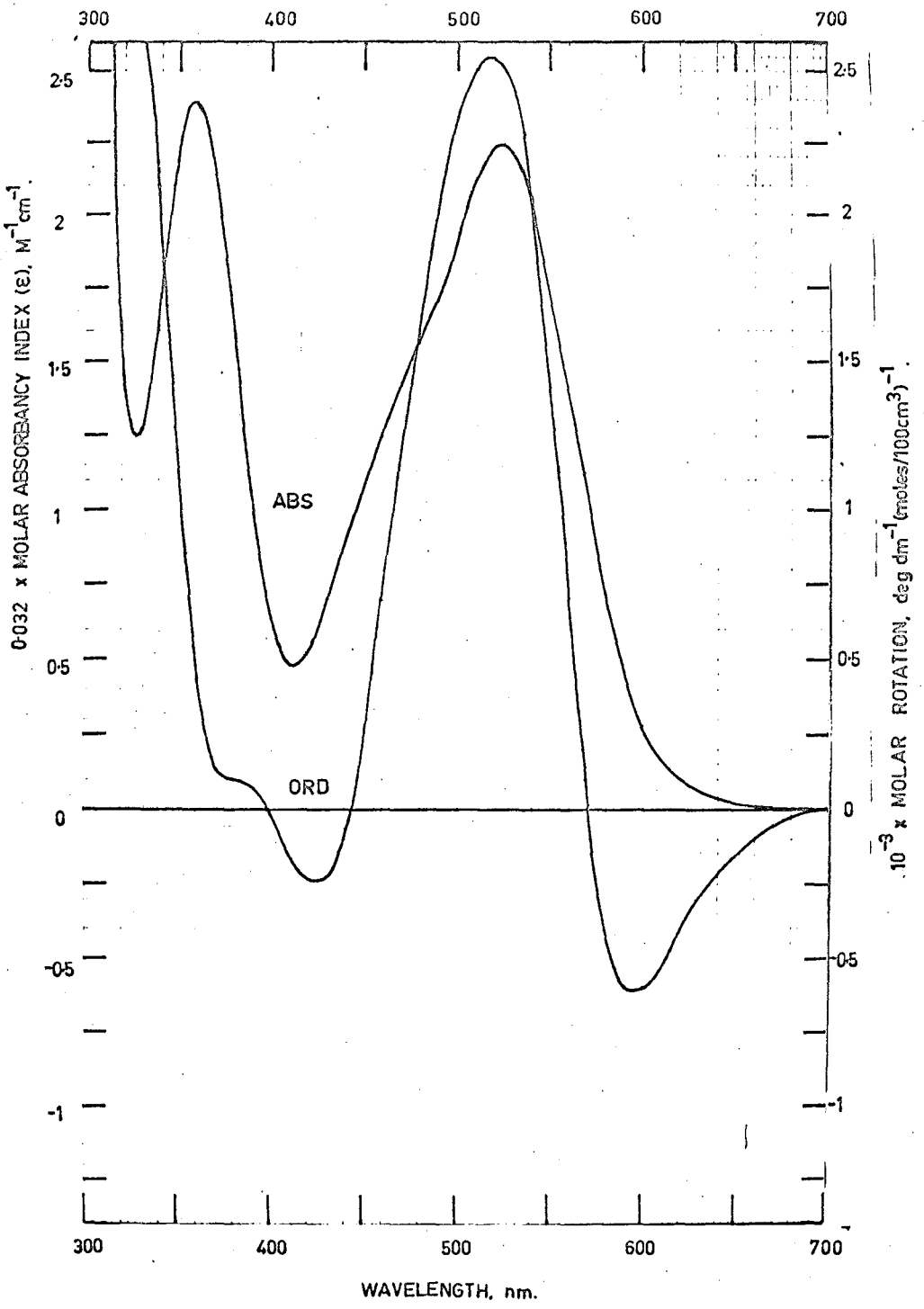


Figure 3.31 Optical rotatory dispersion and visible absorption spectra of (−) − D − $Co(pn)(dien)Cl^{2+}$ in 0.1 F $HClO_4$ at 20-25°.

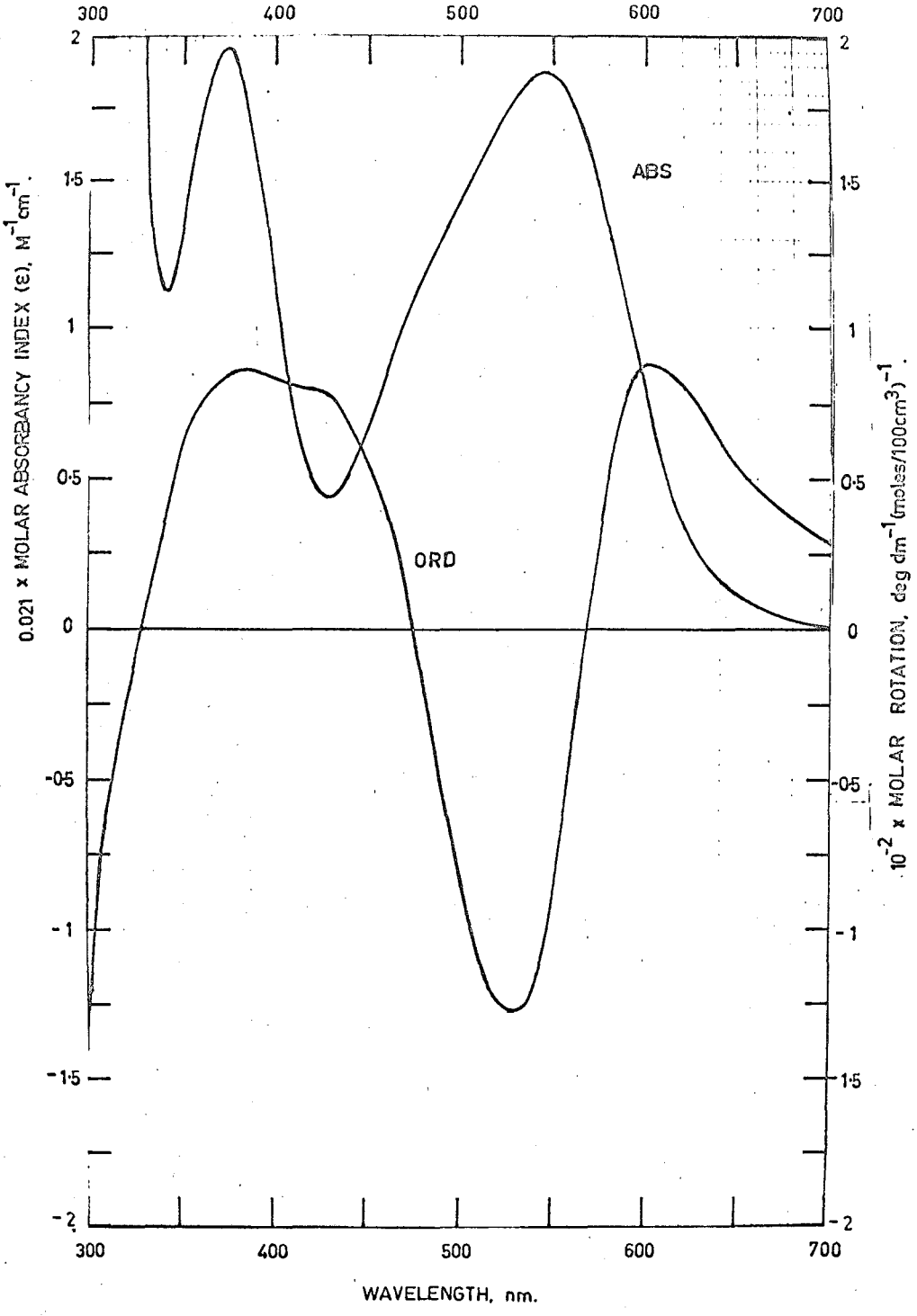


Figure 3.32 Optical rotatory dispersion and visible absorption spectra of (+) - XI - Co(Nip-ibn)(dien)Cl^{2+} in 0.1 F $HClO_4$ at 20-25°.

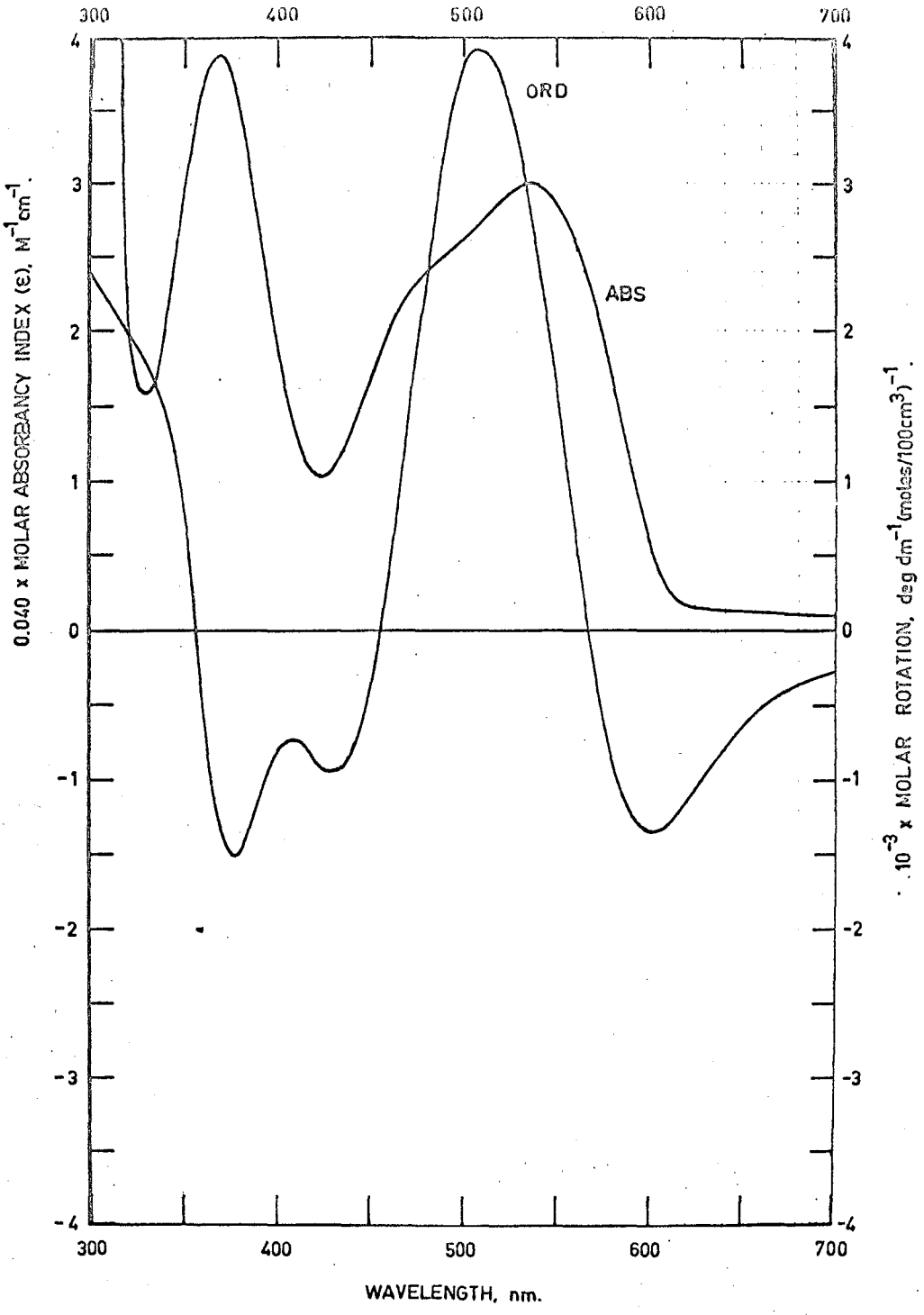


Figure 3.33 Optical rotatory dispersion spectra and visible absorption spectra of (-) - d - $Co(tmd)(dien)Cl^{2+}$ in 0.1 F $HClO_4$ at 20-25°.

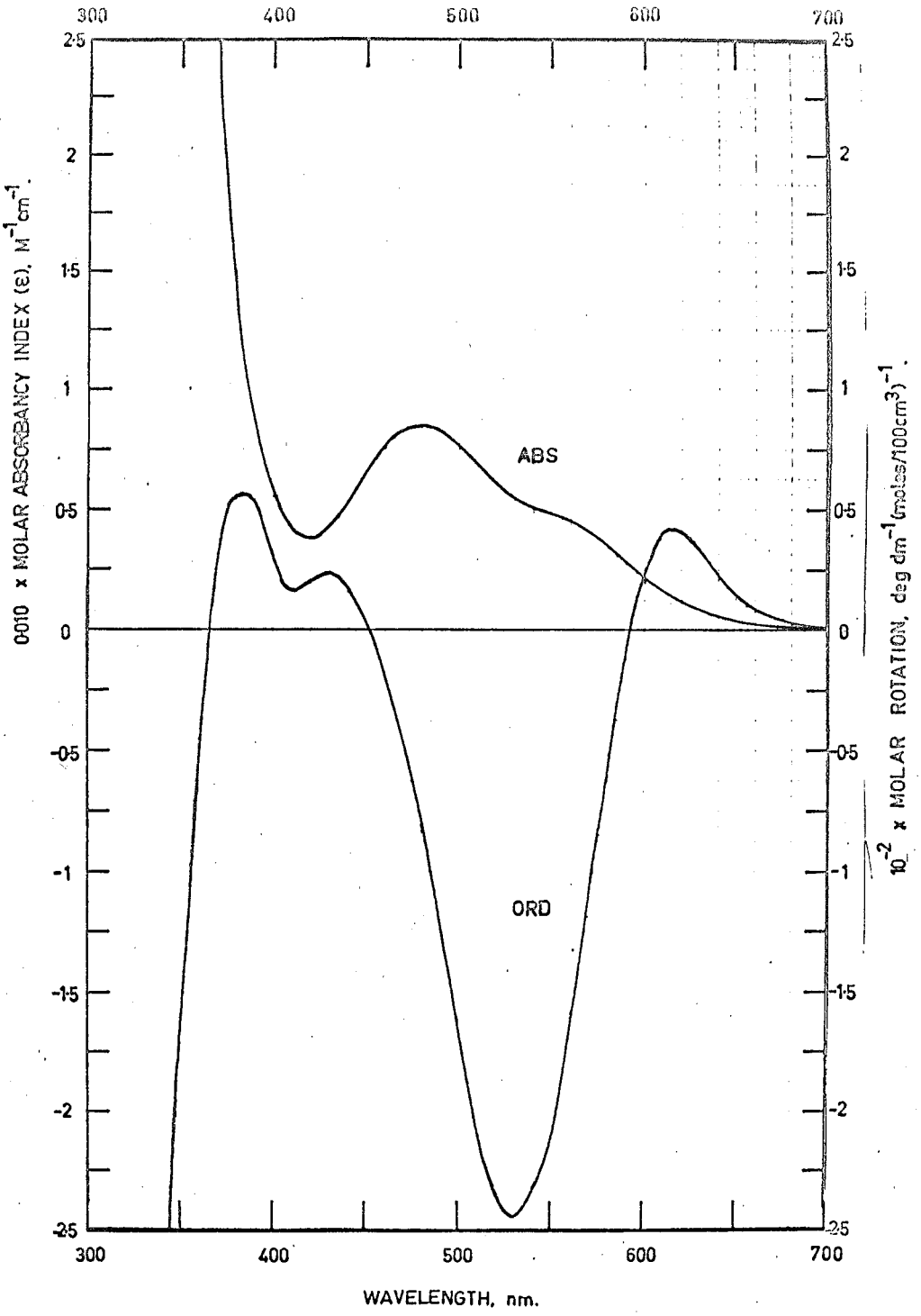


Figure 3.34 Optical rotatory dispersion and visible absorption spectra of (+) - I - Co(Me-tmd)(dien)Cl^{2+} in 0.1 F $HClO_4$ at 20-25°.

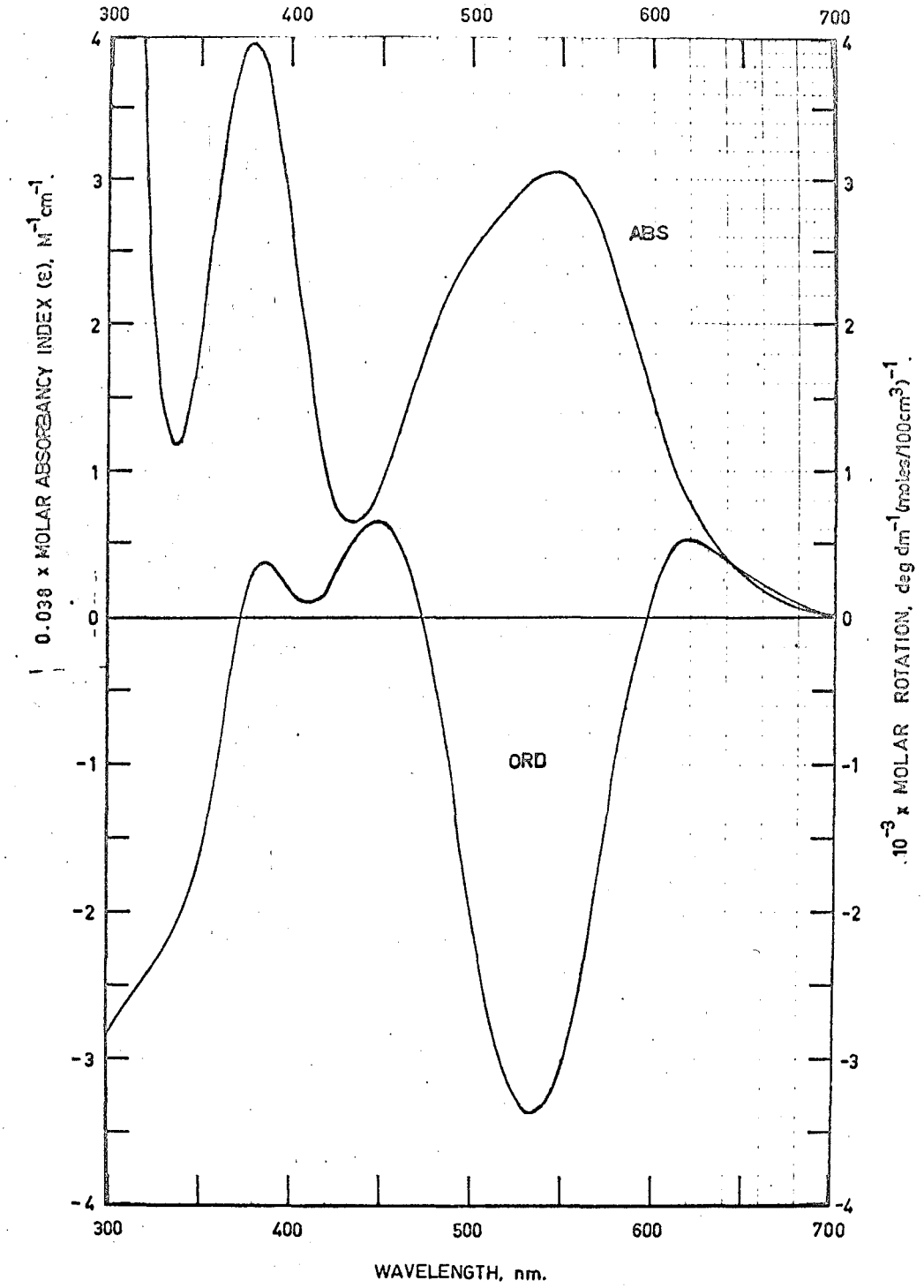


Figure 3.35 Optical rotatory dispersion spectrum and visible absorption spectrum of
(+) - V - $Co(Me\text{-}tmd)(dien)Cl^{2+}$ in 0.1 F $HClO_4$ at 20-25°.

in Fig. 3.37. The spectra of the Σ and η isomers of $Co(2,3\text{-tri})(en)Cl^{2+}$ are presented in Fig. 3.38.

(5) Chloro-nitro Co-crystallising Mixtures

It had been noticed previously (Fig. 3 and 4, reference 30) that the infrared spectra and X-ray powder diffraction patterns of the pairs "γ" and α-[Co(en)(dpt)Cl]$ZnCl_4$ and "ε" and π-[Co(en)(dien)Cl]$ZnCl_4$ were very similar, but there were considerable differences in the visible absorption spectrum. Preliminary single crystal X-ray studies on these compounds showed that the "γ":α (both as the chloride and tetrachlorozincate(II) salts) and "ε":π pairs had identical space groups and unit cell dimensions and were crystallographically indistinguishable (Table 3.4).

An appraisal of the synthetic methods used to prepare the "γ" and "ε" forms revealed that in both cases nitro complexes were used as intermediates and it was apparent from an examination of the visible absorption spectrum that these forms were mixtures of the known α-chloro plus α-nitro and π-chloro plus π-nitro complexes respectively, (Fig. 3.39 and 3.40). Analysis of the spectral parameters of "γ"-[Co(en)(dpt)Cl]$ZnCl_4$ and "ε"-[Co(en)(dien)Cl]$ZnCl_4$ indicate that these are the α-[Co(en)(dpt)Cl]$ZnCl_4$ and π-[Co(en)(dien)Cl]$ZnCl_4$ isomers containing about 27% of the corresponding nitro isomers, respectively (Fig. 3.39 and

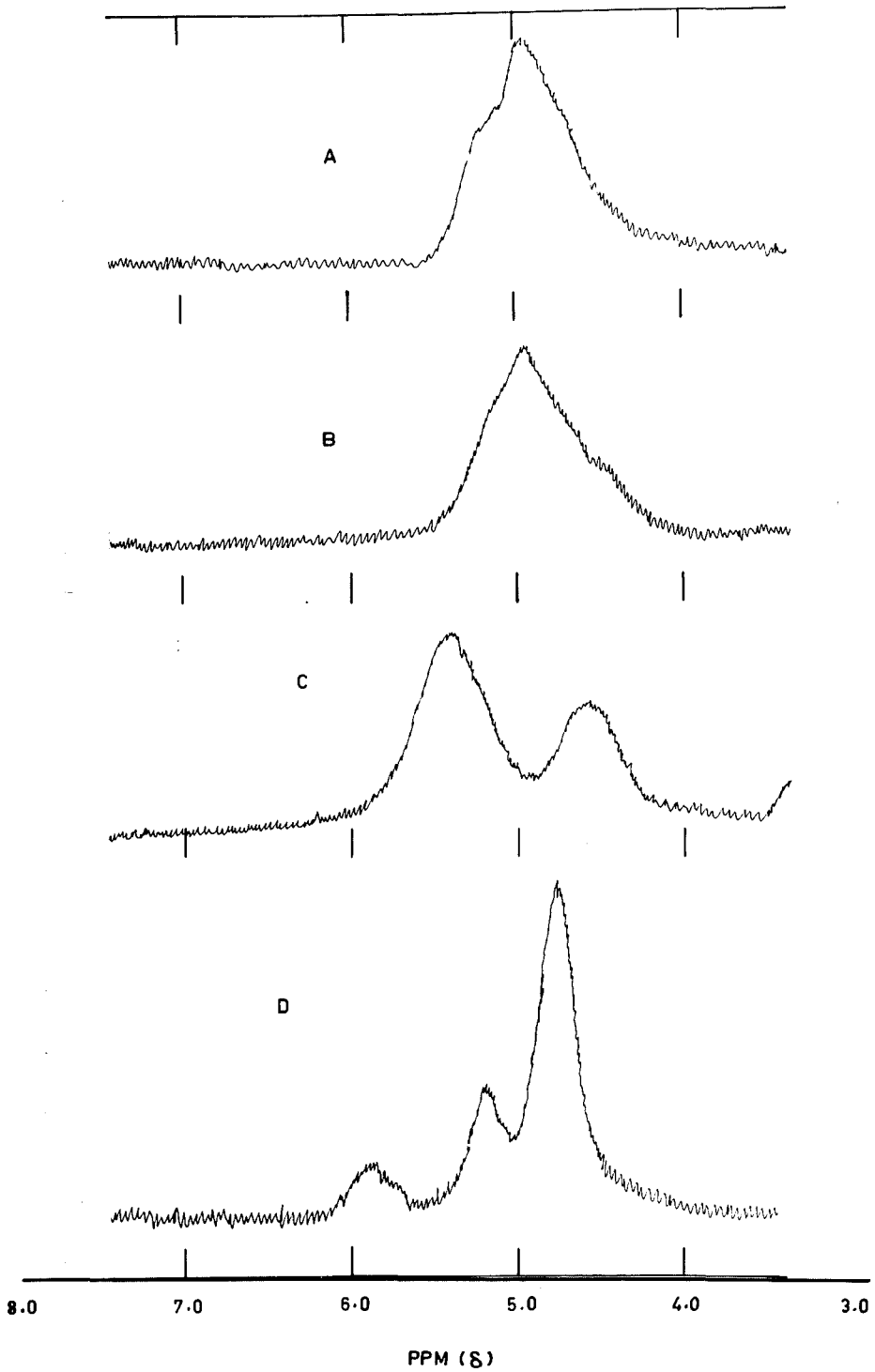


Figure 3.36 The room temperature NMR spectrum of α-$Co(en)(dpt)NO_2^{2+}$ (C), α (A), and β (D) - $Co(en)(dpt)Cl^{2+}$ and "γ-$Co(en)(dpt)Cl^{2+}$" (B) (as the $ZnCl_4^{2-}$ salts) in d_6-DMSO. Only resonances due to NH protons are shown.

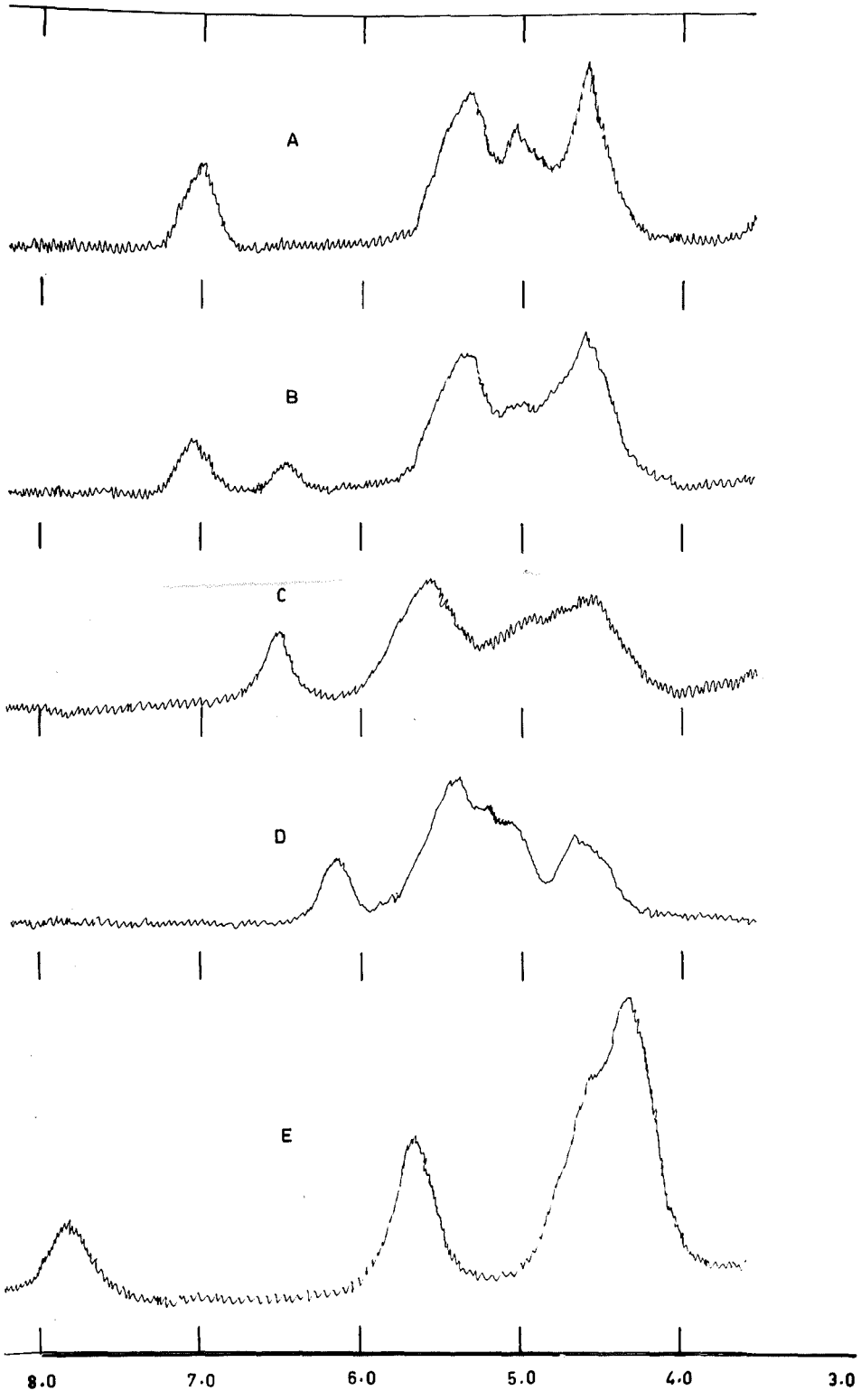


Figure 3.37 The room temperature NMR spectrum of π-Co(en)(dien)NO_2^{2+} (C), π (A), ω (D), and κ (E) - Co(en)(dien)Cl_2^{2+} and $^{u}\varepsilon$-Co(en)(dien)Cl^{2+} (B) (as the $ZnCl_4^{2-}$ salts) in d_6-DMSO. Only resonances due to NH protons are shown.

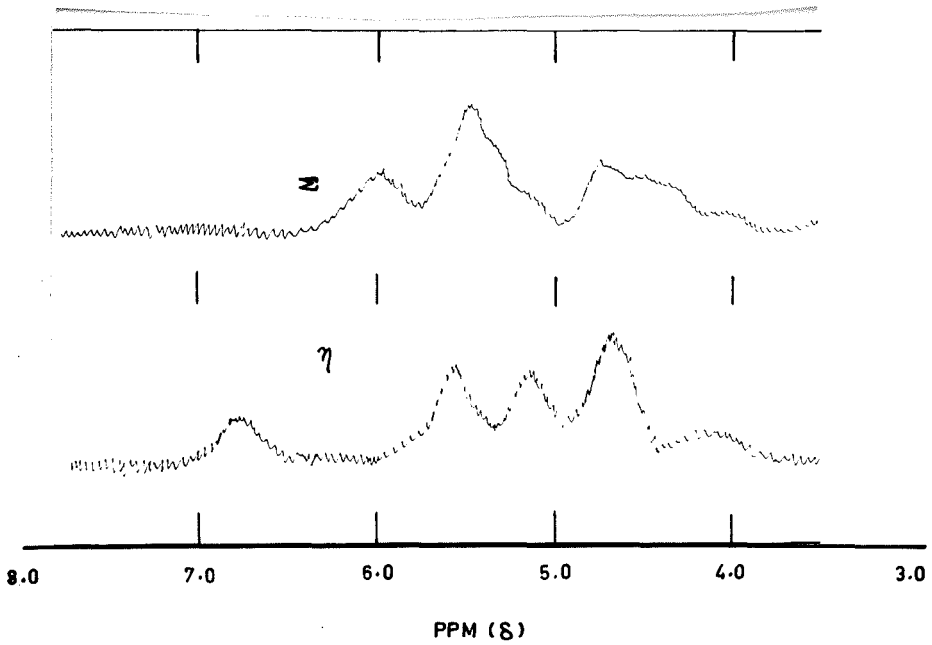


Figure 3.38 The room temperature NMR spectrum of ζ and η $Co(2,3\text{-tri})(en)Cl^{2+}$ (as the $ZnCl_4^{2-}$ salts) in $\underline{d}_6$-DMSO. Only resonances due to NH protons are shown.

3.40).

The differences in the infrared spectrum of the "γ":α and "ε":π pairs are consistent with nitro complex impurity in the α and π isomers (see Fig. 3.1 and Reference 30, Fig. 2). The "γ" and "ε" forms have also been synthesised from α-chloro/α-nitro and π-chloro/π-nitro mixtures (3 parts chloro complex to 1 part nitro complex on a weight basis). After the first recrystallisations, the visible absorption spectral parameters remained essentially constant over five subsequent recrystallisations, indicating constant composition mixtures were crystallising. After five recrystallisations, slight loss of the nitro component was detected, in both cases.

The N.M.R. spectra of π-[Co(en)(dien)X]$ZnCl_4$ (X = Cl^-, NO_2^-) (A and C respectively in Fig. 3.37) and "ε"-[Co(en)(dien)Cl]$ZnCl_4$ (B in Fig. 3.37) in $\underline{d}_6$-DMSO, also indicate that the "ε" isomer is a mixture of the first two components. The "ε" isomer (spectrum B) has bands due to NH protons characteristic of both π-chloro (spectrum A) and π-nitro (spectrum C) in the ratio of <u>ca</u>. 2:1. Similarly, the N.M.R. spectrum of "γ"-[Co(en)(dpt)Cl]$ZnCl_4$ (Spectrum B, Fig. 3.36) is made up of contributions from α-[Co(en)dpt)X]$ZnCl_4$ (X = Cl^-, NO_2^-) (A and C respectively in Fig. 3.36) although the bands are less clearly resolved.

It is perhaps surprising that the chloro and nitro complexes should co-crystallise from aqueous solution, as the tetrachlorozincate(II) salts are not isomorphous in either the dpt or dien systems (Table 3.4). Consequently, it has been unusually difficult to differentiate such mixtures from pure compounds, in these systems where geometric and conformational isomers are common and expected.

From previously published work, it appears that the α-$Co(en)(dpt)NO_2^{2+}$ cation can co-crystallise with the bromo, iodo and isothiocyanato complexes in addition to the chloro, and with a variety of anions (e.g. Cl^-, ClO_4^-, $ZnCl_4^{2-}$, $Zn(NCS)_4^{2-}$, $ZnBr_4^{2-}$). However, π-$Co(en)(dien)NO_2^{2+}$ co-crystallises only with chloro and azido complexes.

Thus only two (α and β) of the four possible $Co(en)(dpt)Cl^{2+}$ isomeric cations have been characterised [30,33,34], both with a peripheral dpt ligand.

Similarly, only three (π, *K* and ω) of the four possible $Co(en)(dien)Cl^{2+}$ isomeric cations have been isolated (Chapter 2).

Preparation of Synthetic Mixtures

α-Chloro(ethylenediamine)(dipropylenetriamine)cobalt(III) Tetrachlorozincate(II)/α-Nitro(ethylenediamine)(dipropylenetriamine)cobalt(III) Tetrachlorozincate(II) Mixture - "γ"-$[Co(en)(dpt)Cl]ZnCl_4$: 0.75 g of α-$[Co(en)(dpt)Cl]ZnCl_4$

and 0.25 g of α-[Co(en)(dpt)NO_2]$ZnCl_4$ were dissolved together in 25 ml of 0.2 F CH_3CO_2H at 40°. 15 ml of 12 F HCl and 2.5 g of $ZnCl_2$ were then added. The product that deposited was collected, washed with 2-propanol and dried with ether. The yield was 77%. This material was recrystallised five times from 25 ml of 0.2 F CH_3CO_2H at 40° by the addition of 12 F HCl (15 ml) and $ZnCl_2$ (2.5 g) and cooling to room temperature. Small samples for absorption spectral measurements were retained after each recrystallisation.

π-Chloro(ethylenediamine)(diethylenetriamine)cobalt(III) Tetrachlorozincate(II)/π-Nitro(ethylenediamine)(diethylene-triamine)cobalt(III) Tetrachlorozincate(II) Mixture - "ε"-[Co(en)(dien)Cl]$ZnCl_4$: A similar method to the above was employed using 0.75 g of π-Co(en)(dien)Cl $ZnCl_4$ and 0.25 g of π-[Co(en)(dien)NO_2]$ZnCl_4$. The yield was 83%.

Single Crystal X-ray Studies: Crystals of α and "γ"-[Co(en)(dpt)Cl]Cl_2, α-[Co(en)(dpt)NO_2]$ZnCl_4$, π, *K* and "ε"-[Co(en)(dien)Cl]$ZnCl_4$, and π and *K*-[Co(en)(dien)NO_2]$ZnCl_4$ were grown from dilute aqueous HCl solutions of the $ZnCl_4^{2-}$ salts. Crystals of α and "γ"- Co(en)(dpt)Cl $ZnCl_4$ were grown from aqueous HCl containing 10% $ZnCl_2$. Unit cell dimensions were calculated from precession photographs collected at ambient temperature and the data are listed in Table 3.4.

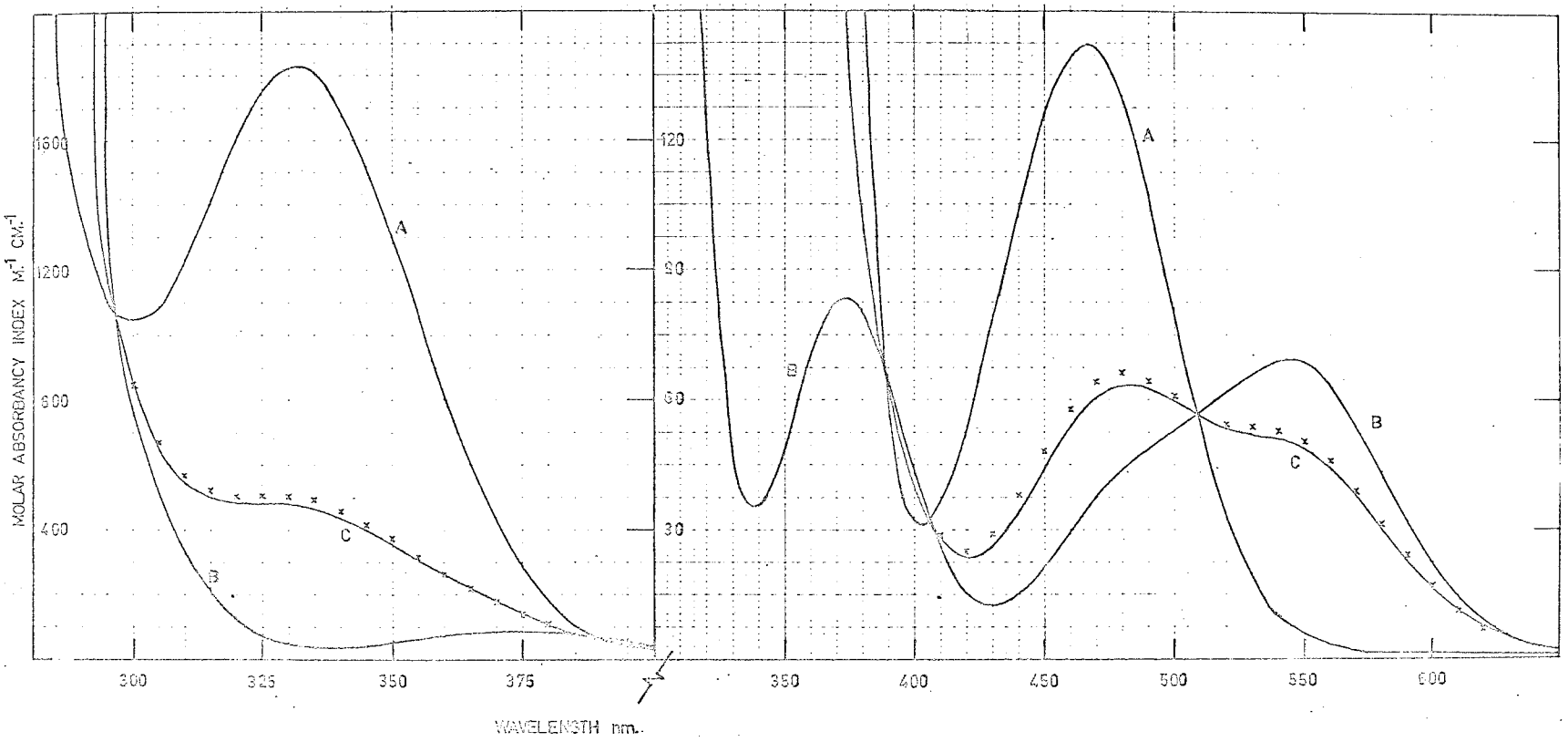


Figure 3.39 The absorption spectrum of α-Co(en)(dpt)NO_2^{2+} (A), α-Co(en)(dpt)Cl^{2+} (B) and "γ"-Co(en)(dpt)Cl^{2+} (C) (after three recrystallisations) in 0.1 F HCl, in the 275-650 nm range. The curve, x x x x, is a theoretical spectrum of (C), generated using the equation $\underline{a}_M(C) = 0.74\underline{a}_M(B) + 0.26\underline{a}_M(A)$.

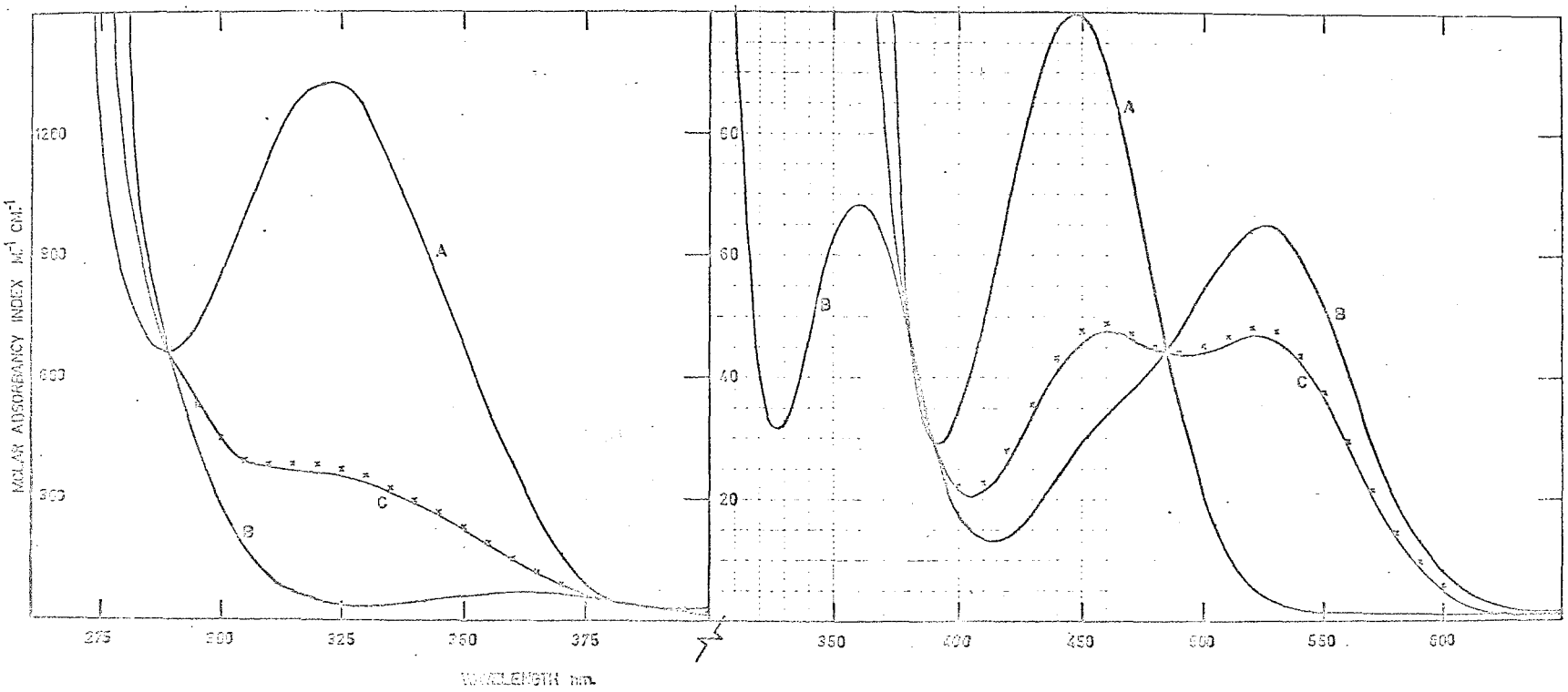


Figure 3.40 The absorption spectrum of π- $Co(en)(dien)NO_2^{2+}$ (A), π-$Co(en)(dien)Cl^{2+}$ (B), and "ε"-$Co(en)(dien)Cl^{2+}$ (C) (after three recrystallisations) in 0.1 F HCl, in the 275-650 nm range. The curve, x x x x, is a theoretical spectrum of (C), generated using the equation $\underline{a}_{\underline{M}}(C) = 0.73\underline{a}_{\underline{M}}(B) + 0.27\underline{a}_{\underline{M}}(A)$.

Nitro-Chloro Mixtures in Other Systems

Similar constant composition crystallising mixtures are observed for the systems studied in Chapter 2. For the $[Co(pn)(dien)Cl]ZnCl_4$ system the "E" and "F" isomers have been shown to have the composition 51% G-$[Co(pn)(dien)Cl]ZnCl_4$ plus 49% G-$[Co(pn)(dien)NO_2]ZnCl_4$ and 44% A-$[Co(pn)(dien)Cl]ZnCl_4$ plus 56% A-$[Co(pn)(dien)NO_2]ZnCl_4$, respectively. The "S" and "T" isomers of $[Co(ibn)(dien)Cl]ZnCl_4$ have been shown to consist of 73% O-$[Co(ibn)(dien)Cl]ZnCl_4$ plus 27% O-$[Co(ibn)(dien)NO_2]ZnCl_4$ and 71% P-$[Co(ibn)(dien)Cl]ZnCl_4$ plus 29% P-$[Co(ibn)(dien)NO_2]ZnCl_4$, respectively. XIV-$[Co(Nip\text{-}ibn)(dien)Cl]ZnCl_4$ is of unknown composition, this being a result of the small number of isomers isolated for the $[Co(Nip\text{-}ibn)(dien)Cl]ZnCl_4$ system. "g"-$[Co(tmd)(dien)Cl]ZnCl_4$ has been shown to have the composition 73% f-$[Co(tmd)(dien)Cl]ZnCl_4$ plus 27% f-$[Co(tmd)(dien)NO_2]ZnCl_4$.

The $[Co(2,3\text{-}tri)(en)Cl]ZnCl_4$ system exhibits three nitro-chloro mixtures: "ρ", "Δ" and "*i*". The composition of each of these is: "ρ" isomer - 69% η-$[Co(2,3\text{-}tri)(en)Cl]ZnCl_4$ plus 31% η-$[Co(2,3\text{-}tri)(en)NO_2]ZnCl_4$: "Δ" isomer - 72% Σ-$[Co(2,3\text{-}tri)(en)NO_2]ZnCl_4$ plus 14% η-$[Co(2,3\text{-}tri)(en)Cl]ZnCl_4$ plus 14% Σ-$[Co(2,3\text{-}tri)(en)Cl]ZnCl_4$: "*i*" isomer - 37% Σ-$[Co(2,3\text{-}tri)(en)NO_2]ZnCl_4$ plus 63% Σ-$[Co(2,3\text{-}tri)(en)Cl]ZnCl_4$.

From these results it appears that the nitro-chloro mixtures form in the ratios nitro:chloro of 1:3, 1:1, 3:1 approximately. Since the parent chloro complexes crystallise in space groups containing 4 molecules in a unit cell, it is not surprising that the above ratios are obtained.

C H A P T E R 4

OCTAHEDRAL COMPLEXES OF THE CHLOROPENTAAMINECOBALT(III) TYPE

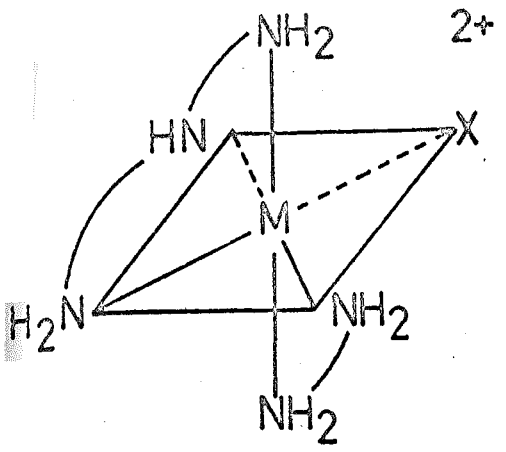
DISCUSSION

DISCUSSION

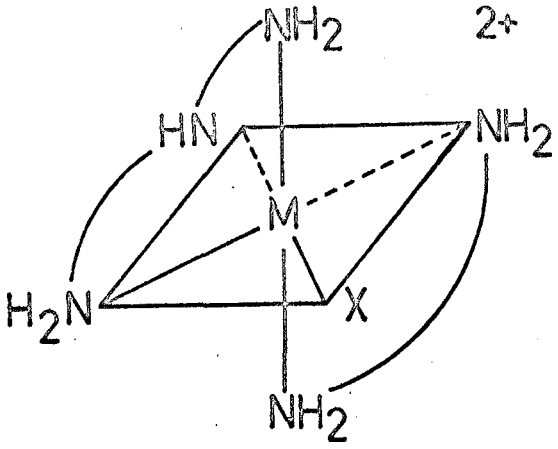
(A) COMPLEXES OF 1,2-DIAMINES WITH DIETHYLENETRIAMINE

(1) Ethylenediamine

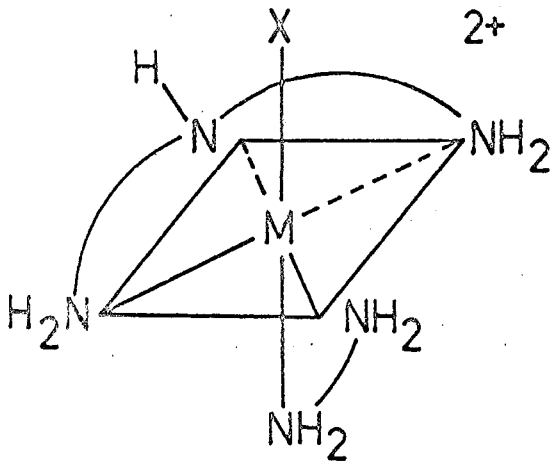
Synthetic Methods: The amount of any particular Co(en)(dien)Cl^{2+} isomer is markedly dependent upon the method of synthesis. The reaction between trans-Co(dien)$(NO_2)_3$ and ethylenediamine[62] gives, presumably, a mixture of the Co(en)(dien)NO_2^{2+} isomers which form nitro complexes (ω, K and π), as the corresponding chloro isomers or constant composition nitro-chloro mixture are isolated as the $ZnCl_4^{2-}$ salts by treating the solution with $HCl/ZnCl_2$. This method of synthesis was originally used by Bosnich and Dwyer[23,24] who isolated the ω chloro chloride as the major product from the nitro intermediates after treatment with 12 F HCl. They tentatively assigned this form to either configuration I or II (Fig. 4.1) and from a single crystal X-ray structure analysis[25] the ω isomer has been shown to have the configuration II. A minor component was also isolated and from its reported visible absorption spectrum, this appears to be the chloro chloride of the K isomer. The chloride salt of the π isomer is apparently too soluble to be isolated by this method. The use of the larger tetrachlorozincate(II) anion, does however, allow their isolation using this route. The π and K isomers have



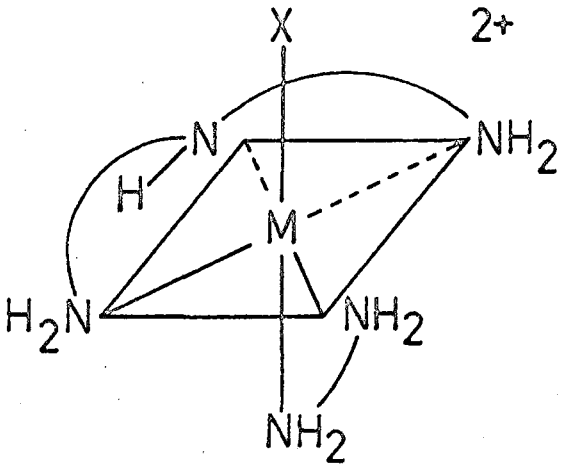
I



II



IIIa



IIIb

Figure 4.1 Possible geometric isomers in a $M(AA)(ABA)X^{2+}$ cation (AA = bidentate linear polyamine, ABA = tridentate linear polyamine).

been shown by single crystal structure analyses (Chapter 5) to have the geometrical configurations I and III_b, respectively (Fig. 4.1). The above reactions contain the dien ligand in the trans or peripheral configuration[23,57-59,62] in the cobalt(III) starting material and the major products are the ω and π isomers. Thus, this reaction sequence involves extensive isomerisation of the diethyleletriamine ligand, as both the π and ω isomers have the cis or facial configuration.

Decomposition of $Co_2(en)_2(dien)_2O_2^{4+}$ [27,67] with HCl containing $ZnCl_2$ forms only the $ZnCl_4^{2-}$ salts of the π and *K* chloro isomers[20] in an approximately 65:35 mixture. This suggests that the parent μ-peroxo complex could be a symmetrical isomeric mixture or contains unsymmetrical pentaamine residues, one with the π and one with the *K* configuration. In a study of the aquation rates of the $Co(en)(dien)Cl^{2+}$ isomers, at present under investigation[37], it has been shown that *K*-$Co(en)(dien)OH_2^{3+}$ isomerises quantitatively to the π isomer ($t_{\frac{1}{2}}$ = 76 min at 75° in 1.0 F $HClO_4$). Thus if the μ-peroxo complex contains the polyamine ligands in the *K* configuration, then at least some of this form would be isomerised to the π form in the course of the decomposition. Further evidence for this hypothesis comes from the fact that refluxing *K*-$[Co(en)(dien)Cl]ZnCl_4$ in 0.05 F HCl for one hour and then

adding 12 F HCl containing $ZnCl_2$ results in about 30% conversion to the π chloro isomer. No trace of the ω isomer has been detected in the products from the decomposition of the μ-peroxo and the aquation studies above[37] show that ω-$Co(en)(dien)Cl^{2+}$ is not isomerised to, or generated from, either of the other isomeric forms.

$Na_3Co(CO_3)_3.3H_2O$[68] reacts with an en/dien mixture forming mixtures of the π-*K* chloro isomers on acidification with $HCl/ZnCl_2$, but yields are low and considerable amounts of hexamine products are produced. An attempt was made to prepare $[Co(en)(dien)I]Cl_2$ using the method of Yalman[73] for the formation of the ammine analog. However, ω-$[Co(en)(dien)Cl]Cl_2.\frac{1}{2}H_2O$ was deposited, and when the solution was acidified with $HCl/ZnCl_2$, mixtures of the π and *K* chloro isomers were isolated.

Several methods were found to interconvert the isomers and these were investigated qualitatively (Chapter 2). Treatment of the pure ω, π and *K* chloro isomers with excess hot NaOH solution and reacidification with HCl to form the chloro $ZnCl_4^{2-}$ salts results in the conversion to a mixture of the π and *K* isomers. It is probable that a mixture of the π and *K* hydroxo ions are formed in the first step and the π and *K* aquo ions, formed in the second step, produce an equilibrium mixture that favours the π isomer due to the isomerisation of *K* aquo to π aquo as already mentioned. In

the analogous Co(trien)(NH_3)Cl^{2+} system, Dwyer[21] has shown that on base hydrolysis a similar result is obtained, e.g. the base hydrolysis of α-Co(trien)(NH_3)Cl^{2+} results in the formation of α (74%), β_2 (24 %) and β_2' (3%) -Co(trien)(NH_3)OH^{2+} ions (α equivalent to π, β_2 equivalent to *K*, β_2' whose equivalent Co(en)(dien)X^{n+} isomer has not yet been isolated). The above hypothesis is supported by the fact that the ω isomer cannot be formed when the synthetic route involves hydroxo complexes.

It is perhaps surprising that the fourth Co(en)(dien)Cl^{2+} (Structure IIIa) isomer has not been detected. In both the Co(en)(dpt)Cl^{2+} [30] and Co(tetren)Cl^{2+} [12,13] systems, inversion from the configuration where the secondary amine proton is remote from the coordinated chloride to the alternate configuration can be achieved quantitatively by base hydrolysis, acidification and subsequent chloride anation of the resulting aquo product. However, the only chloro products so far isolated from the work up of base hydrolysed *K*-Co(en)(dien)Cl^{2+} are the parent or the π-chloro isomer. This latter almost certainly results from isomerisation of the *K* aquo isomer to the π aquo isomer and its subsequent anation. An attempt to prepare this isomer using the method of Dwyer[21], viz. *K*-[Co(en)(dien)Cl]$ZnCl_4$, was hydrolysed at pH 7 for 15 min., reanated using HCl and evaporated to near dryness. The products were separated on

a cation exchange resin, Dowex 50W-X8 20-50 U.S. mesh in the H^+ form, column length 45 cm, diameter 12 mm, by elution with 1.8 F HCl. The only species that were identified were the π and *K* chloro isomers (infrared spectrum), the only effect of this method being considerable *K* to π-chloro isomerisation. In the preparation of these complexes using trans-Co(dien)$(NO_2)_3$ as the starting material, (Methods B and C, Chapter 2), orange-yellow salts were contained in the final crop of complex. Careful re-fractionation of these crops resulted in the partial separation of a species having infrared bands in the 800-950 cm^{-1} region that do not occur in the spectra of the π, ω and *K*-chloro isomers. However, this product has a visible absorption spectrum indicating that it is a nitro-chloro co-crystallising mixture of unknown isomeric composition.

Acido Complexes: Complexes containing the acido ligands Cl^-, Br^-, I^-, NO_2^-, NO_3^-, OH^-, OH_2, HCO_2^-, $CH_3CO_2^-$, φ-CO_2^-, φ-$(CH)_2$-CO_2^-, $CH_3CH(OH)CO_2^-$, N_3^- and NCS^- have been isolated, with a variety of anions, as crystalline salts.

In general, the formation of these complexes from the chloro isomers is obtained with retention of structure. The isomerisation observed in the reaction of π-[Co(en)(dien)Cl]$ZnCl_4$ with HBr producing π and *K*-[Co(en)(dien)Br]$ZnBr_4$ can be explained by an adjustment of the π-*K* aquo equilibrium due to the steric requirement

of the bromide ion. The isomerisation observed in the formation of acido-ω complexes from the *K* isomer for the acido ligand I^- and vice versa for N_3^- (partial), HCO_2^- and $CH_3CO_2^-$, without the detection of π isomer species (through which the course of isomerisation must pass) cannot be explained by the available data for this system.

Spectra: The most noticeable difference between the three isomers of $[Co(en)(dien)Cl]ZnCl_4$ is in the infrared spectrum (Fig. 2.1). Even here, however, there are often only one or two significant bands that allow isomer differentiation. In particular, the bands that serve to distinguish the ω, *K* and π isomers from each other are ω, 820, 610; *K* 920; π 797 cm^{-1}. The infrared spectrum has been used as an index of purity for any particular isomer for the acido ligands Cl^-, Br^-, I^-, NO_2^-, and N_3^-. Complexes containing the other acido groups were converted to the chloro isomers by heating each in 6 F HCl before isomeric assignments could be made. Variation in acido ligand and anion, e.g. from $ZnCl_4^{2-}$ to $2I^-$, can cause considerable band shifts (probably due to changes in non-bonded interactions) even though no configurational change occurs. The spectra of synthetic mixtures of the pure isomers show that it is possible to detect 5-10% of one isomer in the presence of others. Nevertheless, care must be taken in the interpretation of the infrared spectrum, as fractional crystallisation does not always lead to isomer

separation especially for nitro-chloro co-crystallising mixtures and also for π and *K*-$[Co(en)(dien)Cl]ZnCl_4$ mixtures. The separation of the latter mixture is best effected by fractional crystallisation as the perchlorate salts, when *K*-$[Co(en)(dien)Cl](ClO_4)_2$ crystallises first, followed by the $ZnCl_4^{2-}$ salt of the π isomer.

The visible absorption spectra of the π, *K* and ω chloro isomers are quite similar (Fig. 3.1 and 3.2) showing two well defined maxima at about 360 and 520 nm. The 520 nm bands are broad and exhibit a shoulder on the low wavelength side which becomes more pronounced in the order ω < π << *K*. α and β-$Co(tetren)Cl^{2+}$ [12,13] and α and β-$Co(en)(dpt)Cl^{2+}$ [30] show similar pronounced shoulders on the 520 nm band (resolved in the case of β-$Co(tetren)Cl^{2+}$) to the *K* isomer and this is consistent with the fact that all of these complexes contain a "planar" secondary nitrogen atom. The intensities of the acido(ethylenediamine)(diethylenetriamine) complexes at the band maxima are intermediate between those of the corresponding acidopentaammine and acidotetraethylenepentamine complexes, suggesting that the number of chelate rings may be influencing this parameter. In other respects, the spectra of the analogs in these three classes of complex are similar, as would be expected from the fact that in each class the chromophore is CoN_5X^{n+} (Table 3.1).

The visible absorption spectra of π-Cr(en)(dien)Cl^{2+} (Fig. 3.41) shows two well defined maxima at 373 and 512 nm with a prominent shoulder on the low wavelength side of the 512 nm band. The spectra are similar to those obtained for α and β-Cr(tetren)Cl^{2+} [12,13] (Table 3.1).

From recent studies of proton magnetic resonance spectra (pmr) of both monodentate and multidentate cobalt(III) amine complexes, the following simple correlations between the chemical shifts and the environments of amine protons hold[74-77].

(a) Resonances due to protons bonded to a coordinated secondary nitrogen atom are generally at lower field than those due to protons bonded to a coordinated primary nitrogen atom.

(b) Resonances due to protons bonded to a nitrogen atom trans to an acido group are generally upfield from those due to protons bonded to an equivalent nitrogen atom trans to another nitrogen centre.

(c) Resonances due to protons bonded to an "angular" coordinated secondary atom trans to a coordinated primary amine appear at lowest field.

(d) Protons bonded to a nitrogen atom trans to an acido group are generally the most labile.

Based upon this correlation, assignments of resonances consistent with the known stereochemistries of the ω, π and *K* isomers can be made (Fig. 3.37).

For the ω chloro isomer, the resonance at 6.2 ppm is assigned to an "angular" secondary amine proton, that at ~ 5.4 ppm and ~ 4.7 ppm to overlapping primary amine proton signals. These coordinated amine proton resonances correlate to an integral number of protons (integrated peak ratio 1:2:6, total number of protons = 9).

For the π chloro isomer, the resonance at 7.1 ppm is assigned to an "angular" secondary amine proton. The remaining resonances at ~ 5.4 ppm, ~ 5.1 ppm and 4.6 ppm correspond to overlapping primary amine proton signals. Correlation (b) can be applied to the 6.2 ppm and 7.1 ppm resonances of the ω and π chloro isomers respectively. According to the correlation, the ω chloro isomer contains an acido group <u>trans</u> to a coordinated secondary amine proton. This is in agreement with the observed structure[25].

For the *K* chloro isomer, the lowest field signal 7.8 ppm arises from the "planar" secondary amine proton. The resonance at 5.8 ppm arises from the primary amine protons of the ethylenediamine ligand that are <u>trans</u> to the coordinated chloride.

The secondary amine proton resonances for the π and *K* chloro isomers (7.1 ppm and 7.8 ppm, respectively) are similar in position to the equivalent α and β_2 isomers of $Co(trien)(NH_3)Cl^{2+}$ (6.5 ppm and ~ 7 ppm, respectively) except that the resonances for the $Co(en)(dien)Cl^{2+}$ isomers are shifted to lower fields.

In the spectrum of π-$Co(en)(dien)NO_2^{2+}$ (Fig. 3.37, C) the resonance of the secondary amine proton is at 6.5 ppm. This is in accordance with the hypothesis of Hendrickson and Jolly[75] that protons cis to an acido group, X, should resonate at a lower field when X is of lower ligand field strength.

Structures: The structures of the ω[25], π[78] and *K*[78] isomers of $Co(en)(dien)Cl^{2+}$ are II, I and IIIb in Fig. 4.1, respectively. The X-ray structure analyses of the π and *K* chloro isomers are contained in Chapter 5. Consideration of the structure I, II, IIIa and IIIb suggests that the configurations I, II and IIIb should form an interconvertible system via edgewise displacement of the dien or en ligands. This implies that the isomer corresponding to IIIa should not rearrange under conditions where the "planar" secondary amine proton remains intact. Rearrangement is possible, however, if the proton were removed such as in an SN_1CB base hydrolysis mechanism[79]. It is unfortunate that this isomer has not been isolated for this system. However, the above argument has been confirmed by Dwyer[21] using the β_2 and β_2' isomers of $Co(trien)(NH_3)Cl^{2+}$.

Structures IIIa and IIIb can be regarded as cis and trans secondary amine proton forms and similarly related configurations have been postulated in the trans-(O-X)-$Co(dien)(gly)X^+$ ($X = CN^-$) system[80] where two distinct forms

were detected in solution by nuclear magnetic resonance.

Of the structures I-IIIb, only I is potentially optically active. Unfortunately, the resolution of the π chloro isomer has been unsuccessful but the presence of a racemate has been confirmed by X-ray structure analysis (Chapter 5)[78].

The structural pairs I-II and IIIa-IIIb contain the dien ligand in the facial (cis) and peripheral (trans) configurations respectively. Previous workers[58,59,63] have used infrared spectral data to assign the configuration of the dien ligand in monodiethylenetriamine complexes. Of particular significance are the bands in the 800-950 cm^{-1} region where the cis and trans monodiethylenetriamine complexes have 3 and 4 bands respectively. Using this criterion for the assignment of the dien ligand, the infrared spectra of the $[Co(en)(dien)Cl]ZnCl_4$ isomers (Fig. 2.1) suggest that the *K* isomer has the trans arrangement and the π and ω isomers the cis form, assuming the en ligand has little influence on the spectra in the 800-950 cm^{-1} region and regarding the 820 cm^{-1} band of the ω isomer as coming from some other type of infrared active absorption (possibly associated with NH and/or NH_2 groups). In the infrared spectrum of monoethylenediamine complexes such as $Co(en)(NH_3)(NO_2)_3$ and $[Co(en)(NH_3)(OH_2)Cl_2]Cl$, there are two weak bands at 880 and 900 cm^{-1} due to the en ligand and

these probably appear as low intensity shoulders as observed on the dien bands of the $[Co(en)(dien)Cl]ZnCl_4$ isomers.

Of the three chloro isomers isolated, only the π chloro form has been found to be formed or to give a different isomer by chemical conversion. Thus, treatment of the ω isomer with NaOH and then $HCl/ZnCl_2$ yields the π isomer and on refluxing the π isomer in 0.05 F HCl, followed by the addition of 12 F HCl, there is a partial conversion to the *K* isomer. This suggests that the π chloro has the configuration I and this has been confirmed as already mentioned.

From the limited amount of published data (Table 1), it appears that aquation rates (replacement of Cl^- by H_2O in acid solution) are rather insensitive to stereochemistry. Thus, α (or αβR) and β (or αβS) -$Co(tetren)Cl^{2+}$ (related to each other by proton inversion at a "planar" secondary amine centre[15]) aquate with rate constants of 2.2 and 1.3×10^{-5} sec^{-1} in 1 F $HClO_4$ at 70° [36]. Under similar conditions the three $Co(en)(dien)Cl^{2+}$ isomer aquate with rate constants of 8.7 (π), 4.3 (*K*) and 3.7 (ω) $\times 10^{-5}$ sec^{-1} [37]. These data are consistent with the hypothesis that increasing chelation beyond a certain point has little influence on the aquation rate[8,81]. However, the data is inconsistent with the hypothesis that acido ligands trans to coordinated secondary amine groups (as in the ω isomer) aquate more rapidly than those trans to primary amine groups[82].

Base hydrolysis rates (replacement of Cl^- by OH^- in basic solution), however, appear to be much more sensitive to stereochemistry. For the three $Co(en)(dien)Cl^{2+}$ isomers, the relative rates for base hydrolysis[35] are 1 (ω): 5 (π) : 10^4 (K) and the three $Co(tetren)Cl^{2+}$ isomers also have base hydrolysis rates varying over several orders of magnitude[14]. Dwyer[21] has reported that the α isomer of $Co(trien)(NH_3)Cl^{2+}$ base hydrolyses at a rate very much slower than the β_2 and β_2' isomers. Thus it appears that chloropentaaminepolyaminecobalt(III) systems containing a "planar" secondary amine centre have base hydrolysis rate constants several orders of magnitude greater than those complexes where such a configuration is absent. This is supported by the observation that <u>trans</u> and <u>cis</u>-$Co(en)_2NH_3Cl^{2+}$ and β and α-$Co(en)(dpt)Cl^{2+}$ (<u>trans</u> dpt, related by proton inversion) have relative base hydrolysis rate ratios of 1:2.5 and 1:3.9[35], although the magnitudes of the rate constants are about 10^6 times greater in the $Co(en)(dpt)Cl^{2+}$ system[83]. From the above observations it appears that a method of assigning the structures to isomers of more complex systems of the $Co(AA)(ABA)Cl^{2+}$ may be to measure their relative rates of base hydrolysis, with <u>trans</u> configurations reacting faster than <u>cis</u> configurations.

(2) 1,2-propanediamine

Chemical Properties: Seven isomers of $[Co(pn)(dien)Cl]ZnCl_4 . xH_2O$ [A, B, C (1.5 hydrate) D (1.5 hydrate), G, H (dihydrate) and I (dihydrate)] have been isolated by various synthetic routes and of these D-$[Co(pn)(dien)Cl]ZnCl_4 . \frac{3}{2}H_2O$ has been separated into its chiral components. The visible absorption spectra (Fig. 3.3-3.6) indicate that each of these isomers are distinguishable in aqueous acidic solution.

Although the C, D, H and I isomers are hydrated, they appear to be stable hydrated isomers rather than hydrated forms of other isomers. Thus, on recrystallisation, only the parent species are produced.

H-$[Co(pn)(dien)Cl]ZnCl_4 . 2H_2O$ and D-$[Co(pn)(dien)Cl]ZnCl_4 . \frac{3}{2}H_2O$ both retain their configurations in the anhydrous $Zn(NCS)_4^{2-}$ salts and also (for the H isomer) in the anhydrous $CdBr_4^{2-}$ salt. Heating each of the C, D, H and I isomers at 120° for 20 hours results only in dehydration to the anhydrous isomers and recrystallisation of these products reforms the hydrated species.

Interconversions between the isomers can be effected via (a) replacement of Cl^- by Br^-, when D-$[Co(pn)(dien)Cl]ZnCl_4 . \frac{3}{2}H_2O$ gives D-$[Co(pn)(dien)Br]CdBr_4 . \frac{3}{2}H_2O$ and B-$[Co(pn)(dien)Br]CdBr_4$ and (b) base hydrolysis. On reaction with base and acidification and anation with $HCl/ZnCl_2$, the A, "E", "F",

G and H isomers give a mixture of the A and G isomers. Similarly, the B, C, D and I isomers are converted to a mixture of the B and D isomers.

Conversion of the $[Co(pn)(dien)Cl]ZnCl_4.xH_2O$ isomers to $[Co(pn)(dien)NO_2]ZnCl_4.xH_2O$ results in extensive isomerisation. Thus, the A, "E", "F" and G chloro isomers give mixtures of the A and G nitro forms while the D and B chloro isomers give mixtures of the D and B nitro. However, the configuration of the C, H and I chloro isomers are unchanged in the nitro product. The A, G and D, B nitro forms can be separated by refractionation in aqueous acetone/2-propanol of the mixtures described above. Decomposition of the A, B, C, D, G, H and I nitro isomers with HCl followed by the addition of $ZnCl_2$ gives $[Co(pn)(dien)Cl]ZnCl_4.xH_2O$ products with retained configurations.

Replacement of coordinated chloride ligand with iodide, azide or thiocyanate has been successful in these systems. However, no isomerisations as above have been observed in the synthesis of complexes containing these acido groups.

Synthetic Methods: The reaction of trans-$Co(dien)(NO_2)_3$ with 1,2-propanediamine followed by treatment with $HCl/ZnCl_2$ gives all seven isomers in an overall high yield.

However, decomposition of $Co_2(pn)_2(dien)_2O_2^{4+}$ with HCl containing $ZnCl_2$ forms the A, B, D and G isomers with the H isomer as a very minor component. The isolation of the H

isomer (assigned structure II, see later) is contrary to the products obtained in the corresponding (en)(dien) systen synthesis. However ω-$[Co(en)(dien)Cl]ZnCl_4$ may be formed in such small quantities that render it non-detectable.

All of the $[Co(pn)(dien)Cl]ZnCl_4.xH_2O$ isomers were obtained as pure (less than 5-10% isomeric contamination) fractions at various stages of the synthetic methods (tables 2,4, 2.5 and 2.6). Careful fractional crystallisation of the $ZnCl_4^{2-}$ salts of mixtures containing high proportions of a particular isomer were also successful in purifying the major component. For example, fractional crystallisation of the A plus H mixture from fraction 2, crop 6, Table 2.4 gave the pure A isomer. The "E" and "F" isomers (Table 2.5), although both depositing as constant crystallising phases, have been shown to be mixtures of G-$[Co(ph)(dien)Cl]ZnCl_4$ plus G-$[Co(pn)(dien)NO_2]ZnCl_4$ and A-$[Co(pn)(dien)Cl]ZnCl_4$ plus A-$[Co(pn)(dien)NO_2]ZnCl_4$ respectively (Table 3.1).

In all cases, the isomeric purity of any isolated fraction was monitored using the infrared spectrum. Each pure fraction was recrystallised twice from 2 F HCl containing $ZnCl_2$ before recording the characteristic infrared spectrum shown in Fig. 2.2 and 2.3.

Spectra: The visible absorption spectra of the $Co(pn)(dien)Cl^{2+}$ isomeric cations exhibit two well defined maxima at about 520 and 360 nm with prominent shoulders on the 520 nm band (Fig. 3.3-3.5). However, the C isomer

exhibits a shoulder at 327 nm and no 370 nm maximum (Fig. 3.6). The positions and intensities of these bands are comparable to those observed for the $Co(en)(dien)Cl^{2+}$ isomeric cations (Table 3.1).

On comparison of the solution spectra of $Co(AA)(dien)Cl^{2+}$ (AA = en,pn) systems, the ω, H and I isomers show the closest similarity, both in the position and shape of the maxima and in the intensities. There is also a close correspondence of the A and D isomers with π-$Co(en)(dien)Cl^{2+}$ and similarly of the B and G isomers with *K*-$Co(en)(dien)Cl^{2+}$. There is no comparable $Co(en)(dien)Cl^{2+}$ spectra for the C isomer.

Infrared spectra have been the main method of distinguishing between the seven isomers, as was the case in the $[Co(en)(dien)Cl]ZnCl_4$ system. The characteristic bands used in the discrimination of the $[Co(pn)(dien)Cl]ZnCl_4 \cdot xH_2O$ isomers are listed in Table 4.1.

Structural Assignments: In addition to the four basic isomers (Fig. 4.1), each can exist in two forms dependent on the orientation of the asymmetric 1,2-propanediamine ligand. The situation obtained for isomer IIIb is illustrated in Fig. 4.2. Hence, eight isomers should exist for this system and seven of these have been isolated. A similar situation to the above has been predicted in the $Co(Meen)_2Cl_2^+$ [84] and the $Co(N_1\text{-}Mepn)_2Cl_2^+$ [85] systems where only one

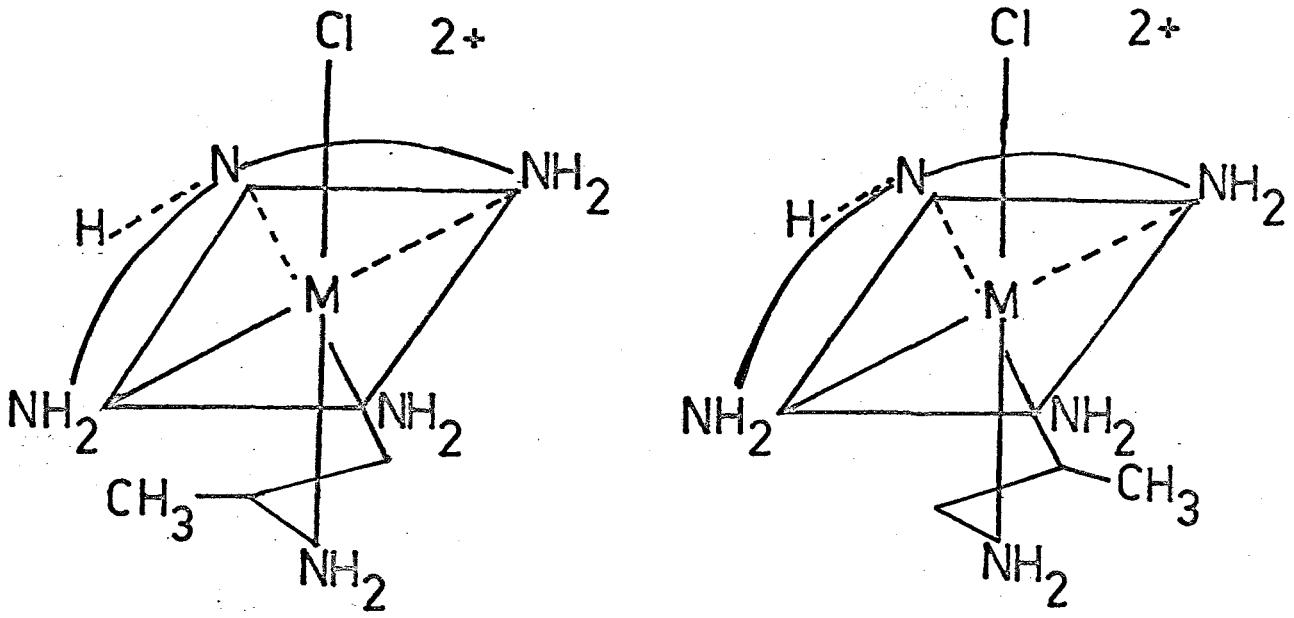


Figure 4.2 Orientations of 1,2-propanediamine ligand in Structure IIIb of $Co(pn)(dien)Cl^{2+}$.

Table 4.1

Characteristic Infrared Frequencies (cm^{-1})

for $[Co(pn)(dien)Cl]ZnCl_4 \cdot xH_2O$ Isomers

A (x=0)	B (x=0)	C (x=1.5)	D (x=1.5)	G (x=0)	H (x=2)	I (x=2)
	1608	1604	1604	1604	1608	1604
1585	1593	1589	1587	1584	1592	1589
1577	1578			1573	1577	1570
	1567	1567	1565	1564	1566	
					1563	
944		946	939	941	940	944
925	923		922	924	915	
910	910	913		912	905	912
896	897	878	888	895	889	876
855	868	867	870	863	871	866
842	842	845	847	841	850	843
832		832				831
		825	822	824	826	

of the possible two trans isomers have been isolated. (Meen = N-methylethylenediamine; N1-Mepn = N-methylpropylenediamine = $CH_3NHCH(CH_3)CH_2NH_2$). The $Co(pn)(dien)Cl^{2+}$ isomeric cations appear to be the first synthesised in which the different orientations of the asymmetric pn ligand have been isolated. By analogy with ω, π and *K*-$Co(en)(dien)Cl^{2+}$, it is probable that the groups A, D; B, G; C; H,I correspond to the four configurations I, IIIb, IIIa and II (Fig. 4.1) respectively. The resolution of D-[Co(pn)(dien)Cl]$ZnCl_4.\frac{3}{2}H_2O$ (Fig. 3.31) assigns this isomer to structure I as this is the only geometric form that is potentially optically active. It is probable that the unsymmetrical 1,2-propanediamine ligand is also resolved but the rotatory strength (ca. 2500° molar rotation) is comparable to that obtained in (-)-d-$Co(tmd)(dien)Cl^{2+}$ (see later) and thus the geometric structure I must be resolved. However the resolution of the A isomer has not been successful.

The assignments of the H, I and B, G isomers to configurations II and IIIb respectively, are based on their similarity with the known ω and *K*-[Co(en)(dien)Cl]$ZnCl_4$ isomers. In addition B-[Co(pn)(dien)Cl]$ZnCl_4$ is isomorphous with *K*-[Co(en)(dien)Cl]$ZnCl_4$ (Tables 3.2 and 3.4).

The visible absorption (Fig. 3.4) and infrared spectrum (Fig. 2.3) of H and I-[Co(pn)(dien)Cl]$ZnCl_4.xH_2O$ suggest a facial dien configuration and the chemical reactions

(slow chloride replacement by NO_2^-, Br^- and NCS^-) parallel those of ω-[Co(en)(dien)Cl]$ZnCl_4$. Similarly, the visible absorption (Fig. 3.5) and infrared spectra (Fig. 2.2, 2.3) of B, G (and C)-[Co(pn)(dien)Cl]$ZnCl_4.xH_2O$ and *K*-[Co(en)(dien)Cl]$ZnCl_4$ (Fig. 3.1) closely correspond. The four bands in the infrared spectrum between 830 and 950 cm^{-1} (superimposed on other CH vibrations due to the methyl group on the pn ligand), together with the broad visible absorption maxima at about 500 nm (Fig. 3.5, 3.6) being characteristic of a peripheral dien configuration[58,59,63].

The C isomer (tentatively assigned to structure IIIa) has only been isolated in medium amounts. This would correspond to the non-observance of this configuration in the $Co(en)(dien)Cl^{2+}$ system and to the low yield of β_2' isomer in the structurally related $Co(trien)(NH_3)Cl^{2+}$ system.[21] The assignment of the C isomer to this configuration is supported by the observation that this form is not isomerised in refluxing 6 F HCl (1 hour) or in reacting with NO_2^-, whereas all other forms (except H, I) undergo at least some stereochemical change. The C to B plus D (IIIa → IIIb + I) isomerisation under basic conditions is possible *via* NH(dien) proton inversion.

The products of base hydrolysis of each isomer of $Co(pn)(dien)Cl^{2+}$ consist of two distinct groups; A plus G and B plus D. Hence, the isomers giving rise to, for

example, an A plus G mixture, must be related by edgewise displacement of isomers arising from one orientation of the asymmetric pn ligand (Fig. 4.2). Similarly the isomers that give a B plus D mixture on base hydrolysis must be related by edgewise displacement of isomers arising from the opposite orientation of the pn ligand above.

By assuming arbitrarly that the B isomer has configuration 1 (Fig. 4.3), then the isomers D and C automatically have the configurations 2 and 3 respectively.

However, isomers H and I cannot be unambiguously assigned from this assumption because edgewise displacement of the pn ligand in structure II can produce isomers of structure I having opposite orientations of the pn ligand, depending on which end of the pn ligand moves (Fig. 4.3). Nevertheless, only one isomer pair (B plus D from I, or A plus G from H) has been detected. Hence it must be assumed that only one end of the pn ligand moves via edgewise displacement, i.e. a stereospecific isomerisation. If it is assumed that the primary amine group remote from the methyl group is the one displaced, then the I isomer can be assigned to 4; Fig. 4.3. It should be noted that these assumptions are by no means established and that they have been made in order to clarify the relationships between the isomers.

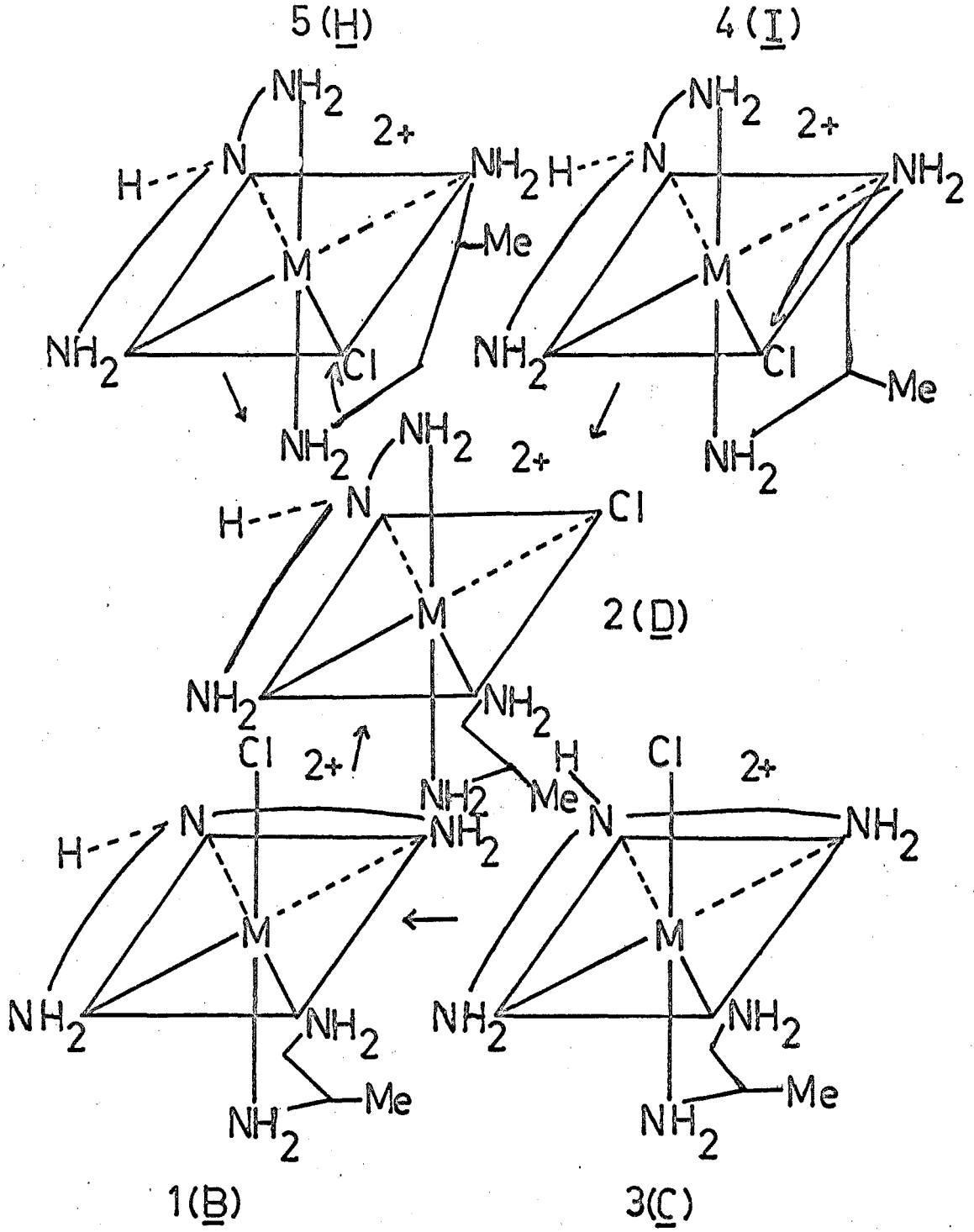


Figure 4.3 Edgewise Displacement of Isomers of $Co(pn)(dien)Cl^{2+}$.

In comparing the $Co(AA)(dien)Cl^{2+}$ (AA = en,pn) systems, there is a notable difference in the configurations of the products from base hydrolysis, acidification and anation with $HCl/ZnCl_2$. All $Co(en)(dien)Cl^{2+}$ isomers give π-$[Co(en)(dien)Cl]ZnCl_4$ (structure I) whereas all $Co(pn)(dien)Cl^{2+}$ isomers give a mixture corresponding to π plus *K* $[Co(en)(dien)Cl]ZnCl_4$. It is probable that under basic conditions, an equilibrium I-IIIb-(IIIa)? mixture is obtained and that the isomers isolated reflect the different positions of the equilibrium, and the relative solubility of the chloro tetrachlorozincate(II) salts. The solubility of the $[Co(en)(dien)Cl]ZnCl_4$ isomers is in the order $\omega \sim \pi < K$. However, for the $[Co(pn)(dien)Cl]ZnCl_4.xH_2O$ isomers the solubility of the pairs A,G and B,D are very similar.

The proposed configurations for the $[Co(pn)(dien)Cl]ZnCl_4.xH_2O$ isomers are summarised in Table 4.18.

(3) Isobutylenediamine

Chemical Properties: Seven isomers of $[Co(ibn)(dien)Cl]ZnCl_4.xH_2O$ [O, P, Q, R, Y (dihydrate), V (dihydrate) and W (1.5 hydrate)] have been isolated by various synthetic routes. The visible absorption spectra (Fig. 3.7, 3.8, 3.9 and 3.10) indicate that each of these isomers is distinguishable in aqueous acidic solution.

Although the U, V and W isomers are hydrated, they

appear to be stable hydrated isomers rather than hydrated forms of other isomers.

W-[Co(ibn)(dien)Cl]$ZnCl_4$.$\frac{3}{2}H_2O$ retains its configuration in the anhydrous $ZnBr_4^{2-}$ salt and heating each of the U, V and W isomers at 120° for 12 hours results only in dehydration to the anhydrous isomers. Recrystallisation of these products reforms the hydrated species.

Interconversions between the isomers can be effected *via* base hydrolysis. On reaction with base and acidification and anation with $HCl/ZnCl_2$, the O, P, "S", "T" and U isomers give a mixture of the O and P isomers. Similarly the Q, R and V isomers are converted to a mixture of the Q and R isomers. Under the same conditions isomer W is converted to a mixture of the W and P isomers.

Conversion of the [Co(ibn)(dien)Cl]$ZnCl_4$.xH_2O isomers to [Co(ibn)(dien)NO_2]$ZnCl_4$.xH_2O results in extensive isomerisation. Thus, the P, "S" and "T" isomers give mixtures of the P and O nitro forms while the Q and R isomers give mixtures of the Q and R nitro. However, the configurations of the O, U, V and W isomers are unchanged in the nitro product. The P, Q and R nitro forms can be separated by fractionation in aqueous acetone/2-propanol of the mixtures described in Chapter 2. Decomposition of the O, P, Q, R, U, V and W nitro isomers with HCl followed by the addition of $ZnCl_2$ gives [Co(ibn)(dien)Cl]$ZnCl_4$.xH_2O

products with retained configurations.

Synthetic Methods: The reaction of trans-$Co(dien)(NO_2)_3$ with isobutylenediamine followed by treatment with $HCl/ZnCl_2$ gives all seven isomers in an overall medium yield.

However, decomposition of $Co_2(ibn)_2(dien)_2O_2^{4+}$ with HCl containing $ZnCl_2$ forms the O, P, Q and R isomers with the V isomer as a very minor component. The isolation of the V isomer parallels the observations in the $[Co(pn)(dien)Cl]ZnCl_4.xH_2O$ system.

All of the $[Co(ibn)(dien)Cl]ZnCl_4.xH_2O$ isomers were obtained as pure (less than 5-10% isomeric contamination) fractions at various stages of the synthetic methods (Tables 2.9, 2.10 and 2.11). Careful fractional crystallisation of the $ZnCl_4^{2-}$ salts of mixtures containing high proportions of a particular isomer were also successful in purifying the major component. For example, fractional crystallisation of the Q plus P mixture from fraction 4, crop 2, Table 2.11, gave the pure Q isomer. The "S" and "T" isomers (Table 2.9), although both depositing as constant crystallising phases, have been shown to be mixtures of O-$[Co(ibn)(dien)Cl]ZnCl_4$ plus O-$[Co(ibn)(dien)NO_2]ZnCl_4$ and P-$[Co(ibn)(dien)Cl]ZnCl_4$ plus P-$[Co(ibn)(dien)NO_2]ZnCl_4$ respectively (Table 3.1).

Each pure chloro isomer was recrystallised twice from

3 F HCl containing $ZnCl_2$ before recording the characteristic infrared spectrum shown in Fig. 2.4 and 2.5.

Spectra: The visible absorption spectra of the Co(ibn)(dien)Cl^{2+} isomeric cations exhibit two well defined maxima at about 510 and 370 nm with prominent shoulders on the 510 nm band (Fig. 3.7, 3.8 and 3.9). However, the W isomer exhibits its maxima at 475 and 346 nm (Fig. 3.10). The positions and intensities of these bands are comparable to those observed for the Co(en)(dien)Cl^{2+} isomeric cations (Table 3.1).

On comparison of the solution spectra of Co(AA)(dien)Cl^{2+} (AA = en,ibn) systems, the ω and V isomers show the closest similarity, both in the position and shape of the maxima and in the intensities. There is also a close correspondence of the Q and O isomers with π-Co(en)(dien)Cl^{2+} and similarly of the P and R isomers with *K*-Co(en)(dien)Cl^{2+}. The U isomer does not appear to be similar to the V isomer but these two isomers have similar reaction products with base and nitro ion. There is no comparable Co(en)(dien)Cl^{2+} spectra for the W isomer.

Infrared spectra have been the main method of distinguishing between the seven isomers, as before. The characteristic bands used in the discrimination of the $[Co(ibn)(dien)Cl]ZnCl_4.xH_2O$ isomers are listed in Table 4.2.

Table 4.2

Characteristic Infrared Frequencies (cm^{-1})

for $[Co(ibn)(dien)Cl]ZnCl_4 \cdot xH_2O$ Isomers

O (x=0)	P (x=0)	Q (x=0)	R (x=0)	U (x=2)	V (x=2)	W (x=1.5)
		1612	1617	1618	1637	1609
1604	1605				1625	1601
1583	1585	1593		1594	1589	1593
1572	1576		1583	1583	1584	1583
1564	1567	1578	1578	1568		1575
			1565			
			1436			
1348						
973	972	974	971	971	970	968
949	945	945	945	948	937	
926	928	928	926	920	921	928
896	897	900	896	901	903	909
					894	895
				888	870	889
868	870	870				871
	865		864	869		862
834	840	843	837		836	836
	801				822	823
795		796	789	794	799	792

Structural Assignments: As for the Co(pn)(dien)Cl^{2+} system, eight isomers should exist for this system and seven of these have been isolated. By analogy with ω, π and *K*-Co(en)(dien)Cl^{2+} it is probable that the groups O,Q; P,R; U,V; W; correspond to the four configurations I, IIIb, II and IIIa respectively.

The assignments of the V; P,R; O,Q isomers to the configurations II; IIIb and I respectively, are based on their similarity with the known ω, *K* and π-[Co(en)(dien)Cl]$ZnCl_4$ isomers.

The visible absorption spectra (Fig. 3.8) of U and V-Co(ibn)(dien)Cl^{2+} suggest a facial dien configuration and the chemical reactions (slow chloride replacement by NO_2^- and change of isomeric composition on base hydrolysis) parallel those of ω-[Co(en)(dien)Cl]$ZnCl_4$. Similarly, the visible absorption spectra of O,Q and P,R correspond closely with that of π-Co(en)(dien)Cl^{2+} and *K*-Co(en)(dien)Cl^{2+} respectively.

The W isomer (tentatively assigned to structure IIIa) has been isolated in relatively large amounts. The assignment of this isomer is supported by the observation that this form is not isomerised in reacting with NO_2^-. The W to W plus P partial isomerisation (IIIa → IIIa + IIIb) under basic conditions is possible *via* NH(dien) proton inversion. It is interesting to note that the amount of

IIIa isomer detected increases as the number of substituents on the carbon atom(s) of the linear diamine increases. This may reflect a change in the position of the II-I-IIIb-IIIa equilibrium.

The products of base hydrolysis of each isomer of $Co(ibn)(dien)Cl^{2+}$ consist of two distinct groups: O plus P and Q plus R. Hence, as is also observed in the $Co(pn)(dien)Cl^{2+}$ system, the isomers giving rise to, for example, an O plus P mixture must be related by edgewise displacement of isomers arising from one orientation of the unsymmetric ibn ligand. By assuming arbitrarily that one of the O, P, Q, R or W isomers has a particular orientation of the ibn ligand, then the remaining isomers automatically have their configurations assigned.

The arguments presented for the $Co(pn)(dien)Cl^{2+}$ isomers are equally applicable in this system. Hence the configuration of the U and V isomers cannot be assigned from the above assumption unless a stereospecific isomerisation is postulated.

In comparing the $Co(AA)(dien)Cl^{2+}$ systems (AA = en,ibn) there is a noticeable difference in the configurations of the products from base hydrolysis. The arguments used for the $Co(pn)(dien)Cl^{2+}$ system are equally applicable here as the solubility of the isomeric pairs, P,O and Q, R, is very similar. The partial isomerisation of the W isomer

indicates a further shift in the postulated I-IIIb-(IIIa?) equilibrium.

The $Co(pn)(dien)Cl^{2+}$ and $Co(ibn)(dien)Cl^{2+}$ systems show many parallel properties and they indicate that the type of isomers formed is not particularly influenced by substituents placed on the diamine ligand.

The proposed configurations for the $[Co(pn)(dien)Cl]ZnCl_4.xH_2O$ isomers are summarised in Table 4.18.

(4) N^1-isopropyl-2-methyl-1,2-propanediamine

Five isomers of $[Co(Nip\text{-}ibn)(dien)Cl]ZnCl_4.xH_2O$ [X, XI(monohydrate) XII, XIII and XV] have been isolated and the asymmetric secondary amine centre of the diamine has been separated into its chiral components in the XI isomer (Fig. 3.32). The visible absorption spectra (Fig. 3.11 and 3.12) indicate that each of these isomers is distinguishable in aqueous acidic solution.

Although the XI isomer is hydrated, it appears to be a stable hydrated isomer rather than a hydrated form of the XIII or XV isomers. Thus, on recrystallisation, only the parent species is produced. Heating the XI isomer at 120^o for 2 hours results in partial decomposition and dehydration to the anhydrous isomer and recrystallisation of the product reforms the hydrated species.

Interconversions between the isomers can be effected by base hydrolysis, the X and XIII isomers giving a mixture of the X and XIII isomers. Similarly, the pure XI and XII isomers give a mixture of the XI and XII isomers, and the "XIV" and XV isomers give a mixture of the "XIV" and XV isomers.

Synthetic Methods: The reaction of trans-$Co(dien)(NO_2)_3$ with N^1-isopropyl-2-methyl-1,2-propanediamine only goes partially to completion and treatment of the resulting solution of $Co(Nip\text{-}ibn)(dien)NO_2^{2+}$ isomers produced only two isomers (X and XI) in a very low yield (3.1%). The reaction is incomplete, probably because the secondary amine centre on the diamine is too unreactive to displace coordinated nitro groups easily.

However, reaction of trans-$Co(dien)Cl_3$ with the diamine and then acidification and anation with $HCl/ZnCl_2$ produces all five known isomers in a reasonable yield (38.4%). Since this reaction proceeds through the intermediate $Co(Nip\text{-}ibn)(dien)OH^{2+}$ at the first step, it is expected that isomers of the type I, IIIa and (IIIb?) (Fig. 4.1) only will be formed.

Only the X, XI and XV isomers of $[Co(Nip\text{-}ibn)(dien)Cl]ZnCl_4.xH_2O$ were obtained as pure (less than 5-10% isomeric contamination) fractions at various stages of the synthetic methods (Tables 2.14 and 2.15).

Careful fractional crystallisation of the $ZnCl_4^{2-}$ salts of mixtures containing high proportions of the XII and XIII isomers were necessary to isolate these isomers. For example, fractional crystallisation of the XII plus XV mixture from fraction 2, crop 4, Table 2.14 gave the pure XII isomer. The "XIV" isomer, although crystallising as a constant crystallising phase is a nitro-chloro mixture of unknown composition. This mixture arises because the starting material in this synthesis contained a considerable amount of trans-$Co(dien)(NO_2)_2Cl$. Each pure chloro isomer was recrystallised twice from 1 F HCl containing $ZnCl_2$ before recording the characteristic infrared spectrum shown in Fig. 2.6 and 2.7.

Spectra: With the exception of the XIII isomer, the visible absorption spectra of the $Co(Nip\text{-}ibn)(dien)Cl^{2+}$ isomeric cations exhibit two well defined maxima at about 375 and 540 nm with prominent shoulders on the 540 nm band for the X and XII isomers (Fig. 3.11 and 3.12). The XIII isomer, however, exhibits the 540 nm maximum only, with a shoulder at 355 nm corresponding approximately to the 375 nm bands obtained for the other isomers. The positions of these bands are comparable to those observed for the $Co(ibn)(dien)Cl^{2+}$ isomeric cations (Table 3.1).

On comparison of the solution spectra of $Co(AA)(dien)Cl^{2+}$ (AA = en, Nip-ibn) systems, the π, XI, XIII and XV isomers

show close similarity in the shape of the observed bands. There is also a close correspondence of the X and XII isomers with the *K* isomer.

Infrared spectra has been the only method of distinguishing between the five isomers. The characteristic bands used in the discrimination of the $[Co(Nip\text{-}ibn)(dien)Cl]ZnCl_4 .xH_2O$ isomers are listed in Table 4.3.

Structural Assignments: As for the previous systems, eight isomers should exist for this system. Under the main synthetic route used to prepare these isomers, viz. use of an intermediate $Co(Nip\text{-}ibn)(dien)OH^{2+}$ species as already mentioned, only structures I and IIIb are expected to be formed assuming that the NH (dien) inversion of IIIa → IIIb is completed during the course of the synthesis. Hence, four isomers would be expected from the synthetic routes used. By similarity with the visible absorption spectra of π and *K*-$Co(en)(dien)Cl^{2+}$, it is probable that the groups XI, XIII, XV; X, XII; correspond to configurations I and IIIb respectively. However, this assigns three structure I isomers when only two should exist. By considering models of the cation (I), it can be seen that it is possible for the N-isopropyl group to be restricted into two distinctive "rotational" isomers - (a) with an isopropyl methyl group "trapped" between the two methyl groups at the 2 position of the isobutylenediamine parent or (b) with the hydrogen atom

Table 4.3

Characteristic Infrared Frequencies (cm^{-1})

of $[Co(Nip\text{-}ibn)(dien)Cl]ZnCl_4.xH_2O$ Isomers

X	XI	XII	XIII	XV
	1628			
	1625			
	1610			
1594	1594	1598		
1581		1583	1584	1583
			1578	1576
			1568	1566
		997	995	991
985	986	987	984	985
956	950	957	953	955
947	942	942	944	948
935		937		
932	923	927	924	927
		918		
900	905	907	906	907

attached to the central carbon atom of the isopropyl group in the position described in (a). Interconversion between these two forms would require large steric force barriers to be overcome. This is supported by the similarity of the XIII and XV isomer infrared spectra and by the marked difference in their visible absorption spectra, as already mentioned. Thus, four structure I isomers would be expected in this system but only three have been isolated. Similarly, four structure IIIb isomers would be expected but only two have been isolated.

The products of base hydrolysis of each isomer of $Co(Nip\text{-}ibn)(dien)Cl^{2+}$ consists of three distinct groups: X plus XIII; XI plus XII; XV. The groups, therefore, must be related by edgewise displacement of isomers arising from one orientation of the asymmetric Nip-ibn ligand (c.f. Fig. 4.2), as is the case in the previous systems.

The proposed configurations for the $[Co(Nip\text{-}ibn)(dien)Cl]ZnCl_4.xH_2O$ isomers are summarised in Table 4.18.

(5) Meso-Stilbenediamine:

Four isomers of $[Co(stien)(dien)Cl]ZnCl_4$ (o, p, q, r) have been isolated and the visible absorption spectra indicate that each of these isomers is distinguishable in aqueous acidic solution (Fig. 3.13 and 3.14).

The isomerisation q → p on the change of acido group from Cl^- to Br^- has been observed.

Synthetic Method: The reaction of trans-$Co(dien)Cl_3$ with meso-stilbenediamine followed by acidification and anation with $HCl/ZnCl_2$ results in the formation of all four isomers in high yield.

Since the reaction is assisted by the addition of sodium hydroxide, the reaction proceeds through the intermediate $Co(stien)(dien)OH^{2+}$ and thus isomers of structures I, IIIb and (IIIa?) are the most likely to be formed.

All of the isomers were obtained as pure (less than 5-10% isomeric impurity) fractions at various stages of the synthetic method. Each pure fraction was recrystallised twice from 50% aqueous methanol containing HCl and $ZnCl_2$ before recording the characteristic infrared spectrum shown in Fig. 2.8.

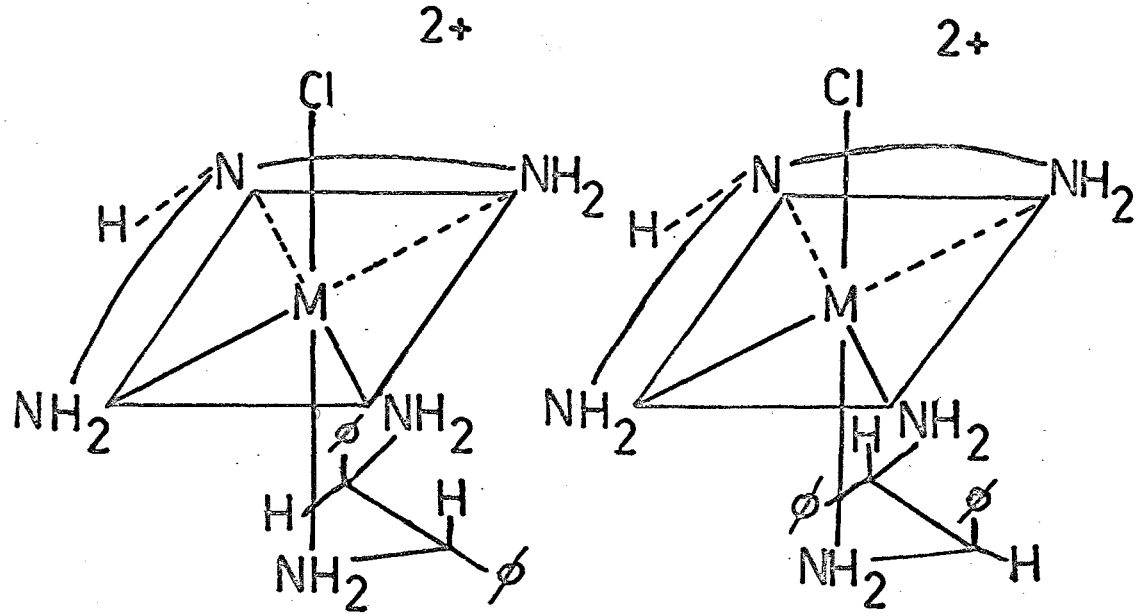
Spectra: The visible absorption spectra of the $Co(stien)(dien)Cl^{2+}$ isomeric cations exhibit a well defined maxima at about 530 nm with prominent shoulders on this band for the q and r isomers. In addition, each exhibits a shoulder at the onset of the charge-transfer region at about 370 nm, the absorption being just resolved for the o isomer (Fig. 3.13, 3.14).

On comparison of the solution spectra of $Co(AA)(dien)Cl^{2+}$ (AA = en, stien)systems, the π, o and p

isomers show close similarity, both in the position and shape of the maxima. There is also a close correspondence between the *K*, q and r isomers. Infrared spectra has been the main method of distinguishing between the four isomers. The characteristic bands used in the discrimination of the $[Co(stien)(dien)Cl]ZnCl_4$ isomers are listed in Table 4.4.

Structural Assignments: As for the previous system, the synthetic route involves the intermediate $Co(stien)(dien)OH^{2+}$ species as already mentioned. Hence only isomers having the structures I and IIIb can be formed assuming that the NH(dien) inversion of IIIa → IIIb is completed during the course of the synthesis. However, two modifications of the structures I and IIIb exist depending on whether the phenyl groups are (a) above or below the plane defined by the NH(dien),Co and primary amines of the stien ligand in structure I (Fig. 4.4), or (b) above or below the plane defined by the NH(dien), Cl and Cl in structure IIIb. Hence, four isomers of $[Co(stien)(dien)Cl]ZnCl_4$ of structures I and IIIb may exist and all of these have been isolated. From the similarity with the visible absorption spectra of π and *K*-$Co(en)(dien)Cl^{2+}$, it is probable that the groups o, p; q, r correspond to structures I and IIIb respectively.

The observed isomerisation q → p on change of acido ligand from Cl^- to Br^- indicates that these two isomers are linked by edgewise displacement of the dien ligand. It is



1 2

Figure 4.4 Possible orientations of meso - stilbenediamine in Structure IIIb of $Co(stien)(ABA)Cl^{2+}$ (ABA = dien, dpt).

Table 4.4

Characteristic Infrared Frequencies (cm^{-1})

of $[Co(stien)(dien)Cl]ZnCl_4$ Isomers

o	p	q	r
	1595	1602	1600
1587	1586	1578	1580
1551	1577		1564
791	797	795	792
778	784		
767	768	758	757
748	751		
	745		735
710	706	710	
703	702	705	702

inferred that the o and r isomers are similarly linked, but this has not been confirmed. This situation is illustrated in Fig. 4.5. However, the exact assignments are unknown.

The proposed configurations for the [Co(stien)(dien)Cl] $ZnCl_4$ isomers are summarised in Table 4.18.

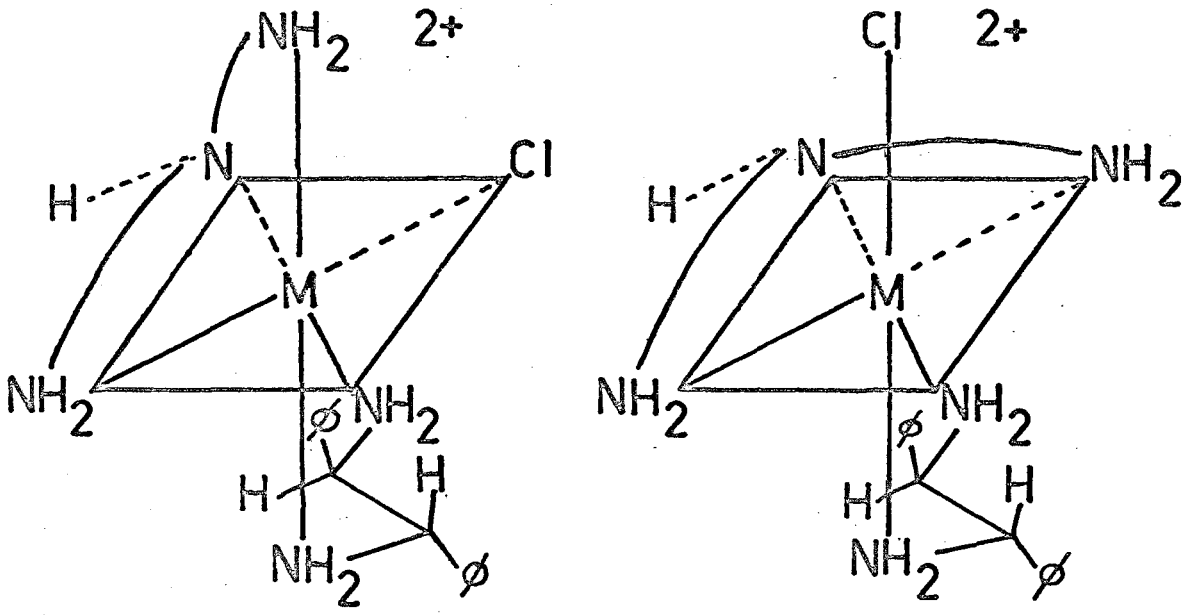
(B) COMPLEXES OF 1,3-DIAMINES WITH DIETHYLENETRIAMINE

(1) 1,3-propanediamine

Chemical Properties: Seven solid state forms of $[Co(tmd)(dien)Cl]ZnCl_4.xH_2O$ have been detected but the visible absorption spectra (Fig. 3.15 and 3.16) indicate that only four groups, viz. d, e, f; a, b; c and h are distinguishable in aqueous acidic solution.

Although the e and h forms are monohydrates, and e can be dehydrated to give d, they appear to be separate isomers rather than hydrated forms of another isomer. Thus, the d form does not yield e (but only itself) on recrystallisation from aqueous HCl containing $ZnCl_2$, and a distinct e-$[Co(tmd)(dien)Cl](ClO_4)_2$ can be prepared. However, heating the e and f forms at 100° for 12 hours results in complete conversion to the stable d isomer.

The h-$[Co(tmd)(dien)Cl]ZnCl_4.H_2O$ isomer also retains its configuration in the anhydrous $CdBr_4^{2-}$ salts and is one



p q

Figure 4.5 Possible relationship between the p and q isomers of $Co(stien)(dien)Cl^{2+}$.

of the three forms (the others being a and d) that form bromo complexes. Heating the h (monohydrate) form at 120° for 12 hours results only in dehydration to give the anhydrous h isomer and recrystallisation of this reforms the monohydrate.

Interconversion between the sets of isomers can be effected via replacement of Cl^- by Br^- when a-$[Co(tmd)(dien)Cl]ZnCl_4$ isomerises nearly completely to d-$[Co(tmd)(dien)Br]CdBr_4$, or by base hydrolysis. In fact, on reaction with base and acidification and anation with $HCl/ZnCl_2$, all isomeric forms of $[Co(tmd)(dien)Cl]ZnCl_4.xH_2O$ give the a isomer.

Conversion of the $[Co(tmd)(dien)Cl]ZnCl_4.xH_2O$ isomers to $[Co(tmd)(dien)NO_2]ZnCl_4$ results in extensive isomerisation (Fig. 4.6). Thus the d, e and f chloro isomers give only the f nitro, the a and b chloro isomers give the b nitro, while the configurations of the c and h forms are unchanged in the nitro product. Decomposition of the f, b, c and h nitro isomers with HCl followed by the addition of $ZnCl_2$ gives chloro products with retained configuration, except for f-$[Co(tmd)(dien)NO_2]ZnCl_4$, where the d chloro isomer is formed.

Replacement of the coordinated chloride ligand with iodide or thiocyanate has not been successful in this system. With iodide, there is extensive formation of Co^{2+} and I_2 and with thiocyanate, $Co(dien)(NCS)_3$ is the only

identifiable product.

Synthetic Methods: The amount of any particular $[Co(tmd)(dien)Cl]ZnCl_4.xH_2O$ isomer produced is markedly dependent upon the method of synthesis used. The reaction between trans-$Co(dien)(NO_2)_3$ and 1,3-propanediamine, followed by treatment with $HCl/ZnCl_2$ gives seven isomers, but the a form is only detected in small amounts (Tables 2.20 and 2.21). The isolation of the e isomer is perhaps surprising as the only solid state nitro isomer obtained from this chloro complex has the f configuration. The e form is assigned to a ring conformational isomer of the stable d isomer (see later) and it is possible that this conformation exists in solution, the isolation as chloro complex being facilitated by the relative insolubility of the $ZnCl_4^{2-}$ salt.

Decomposition of $Co_2(tmd)_2(dien)_2O_2^{4+}$ in HCl containing $ZnCl_2$ forms the a, b, c, d and e chloro pentaamine isomers.

All of the isomers except c were obtained as pure (less than 5-10% isomeric contamination) fractions at various stages of the synthetic methods (Tables 2.19-2.21). Careful fractional crystallisation of the $ZnCl_4^{2-}$ salts of mixtures containing high proportions of a particular isomer were also successful in purifying the major component. For example, fractional crystallisation of the c plus f mixture from fraction 1, crop 7, Table 2.21 gave the pure c isomer.

In the case of the h isomer, excellent separation was achieved via the di-iodide salt. The "g" isomer (Table 3.1), although depositing as a constant crystallising phase, is shown to be a mixture of f-$[Co(tmd)(dien)NO_2]ZnCl_4$ and f-$[Co(tmd)(dien)Cl]ZnCl_4$ in the approximate ratio of 1:3.

In all cases, the isomeric purity of any isolated fraction was monitored using the infrared spectrum. Each pure fraction was recrystallised twice from 2 F HCl containing $ZnCl_2$ before recording the characteristic infrared spectrum shown in Fig. 2.9 and 2.10.

Spectra: The visible absorption spectra of the $Co(tmd)(dien)Cl^{2+}$ isomeric cations exhibit two well defined maxima at about 370 and 520 nm with prominent shoulders on the 520 nm band (Fig. 3.15 and 3.16, Table 3.1).

It has been previously mentioned that the seven solid state isomers of $[Co(tmd)(dien)Cl]ZnCl_4.xH_2O$ can be divided into four groups d, e, f; a, b; h; c with distinguishable solution spectra.

On comparison of the solution spectra in the $Co(AA)(dien)Cl^{2+}$ (AA = en, tmd) systems the ω and h isomers show the closest similarity, both in the position of the maxima and the intensities. There is also a close correspondence with the d, e, f group and π-$Co(en)(dien)Cl^{2+}$.

Infrared spectra have been the main method of distinguishing between the solid state isomers. The characteristic

bands used in the discrimination of these isomers are listed in Table 4.5.

Structural Assignments: Within the structures I, II, IIIa and IIIb there exists the possibility of a variety of ring conformations within the six-membered tmd chelate ring. Such conformational isomerism has been established in the $Cr(en)_3^{3+}$ system[86] and although no ring conformers of $Co(tmd)_3^{3+}$ have been reported (all of the tmd rings in $[Co(tmd)_3]Br_3.H_2O$ adopt the preferred chair conformation[87]), the abnormally rapid ($t_{\frac{1}{2}}$ = 13 sec. at 25° [88]) aquation of trans-$Co(tmd)_2Cl_2^+$ in aqueous acidic solution could be explained by the formation of boat or twist-boat ring conformations in solution[59a]. (Both of the tmd rings in solid trans-$[Co(tmd)_2Cl_2]ClHCl.2H_2O$ adopt the chair conformation[89].)

If only chair and twist-boat six-membered ring conformations are considered, there are 16 possible configurations in this system. The basic set of eight configurations, e.g. I-chair, I-twist-boat, is doubled because the tmd ring can lie, in the case of structure IIIa, above or below the plane defined by the Co, Cl and NH(dien) groups (Fig. 4.7). The crystal structures of the α and γ forms of Cu(tetramine)$(NCS)_2$ indicate that the six-membered (middle) aliphatic chelate rings have "chair" conformations above and below the plane defined by the Cu and N atoms of the rings. In the $Co(tmd)(dien)Cl^{2+}$ system, the four distinguishable

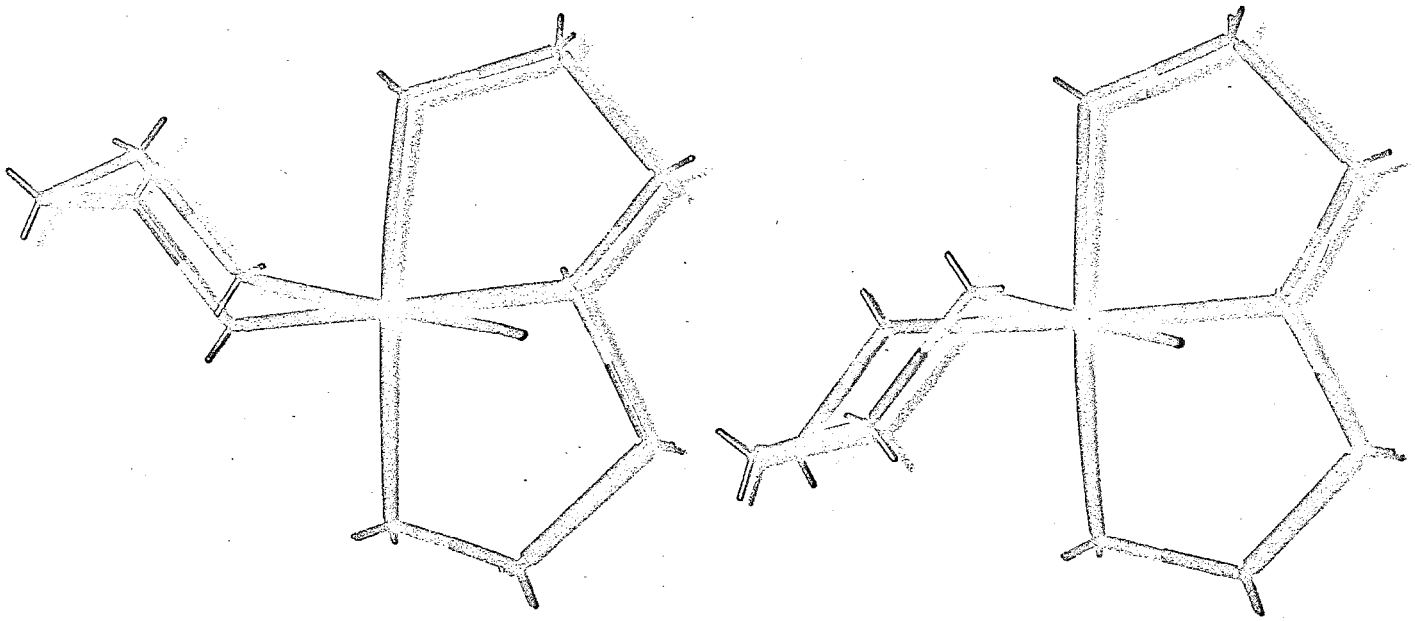


Figure 4.7 Possible orientations of the chair tmd ring in structure IIIb of $Co(tmd)(dien)Cl^{2+}$.

Table 4.5

Characteristic Infrared Frequencies (cm^{-1}) for the $[Co(tmd)(dien)Cl]ZnCl_4 \cdot xH_2O$ Isomers

a	b	c	d	e (x=1)	f	h (x=1)
1597	1597	1590	1596	1597	1610	1600
1581	1575	1580	1577	1579	1583	1579
1569	1569		1554	1570		1566
					954	
922	930	933	943	936	936	926
913					920	899
893	892	896	893	896	887	882
863	860	870	864	871	866	860
834	832	843				
		778	784	796	796	786
		768				
686		684				
673	667		664	664	670	619

groups (d, e, f; a, b; h; c) are believed to correspond to the four structures I, IIIb, II and IIIa, respectively, with d; a,b; h and c as the thermally stable forms.

The resolution of d-[Co(tmd)(dien)Cl]$ZnCl_4$ unambiguously assigns this isomer to structure I as this is the only geometric form that is potentially optically active (Fig. 3.33). The tmd ring probably adopts a chair configuration and models show that the conformation adjacent to the coordinated acido ligand to be the least strained. The thermally unstable e and f isomers (also assigned to I) are most likely to have other tmd ring conformations.

The assignment of the h and a,b isomers to configurations II and IIIb respectively, are based on their similarity with the known ω (II) and *K* (IIIb) [Co(en)(dien)Cl]$ZnCl_4$ isomers (Chapter 5).

The visible absorption (Fig. 3.15) and infrared spectrum (Fig. 2.10) of the h chloro isomer suggest a facial dien configuration and the chemical reactions (slow chloride replacement by NO_2^- or Br^-) parallel that of ω-[Co(en)(dien)Cl]$ZnCl_4$. Similarly, the visible absorption (Fig. 3.16) and infrared spectra (Fig. 2.9) of the a, b (and c)-[Co(tmd)(dien)Cl]$ZnCl_4$ and *K*-[Co(en)(dien)Cl]$ZnCl_4$ closely correspond.

The a, b pair (assigned to IIIb), have identical solution spectra but are thermally non-interconvertible.

They probably correspond to chair tmd ring conformations on either side of the Co, Cl, NH(dien) plane, as illustrated in Fig. 4.7.

The c-$[Co(tmd)(dien)Cl]ZnCl_4$ isomer (tentatively assigned to structure IIIa) has only been isolated in small amounts. This assignment is supported by the observation that this form is not isomerised in refluxing 6 F HCl (30 min.), whereas all other forms in this series (except h) undergo at least some stereochemical change. The c to a isomerisation (IIIa → IIIb) under basic conditions is possible via NH(dien) inversion.

In comparing the $Co(AA)(dien)Cl^{2+}$ (AA = en, tmd) systems, one notable difference is the configuration of the major product resulting from base hydrolysis, acidification and anation with $HCl/ZnCl_2$. All of the $Co(en)(dien)Cl^{2+}$ isomers give π-$[Co(en)(dien)Cl]ZnCl_4$ (structure I), whereas all of the $Co(tmd)(dien)Cl^{2+}$ isomers give a-$[Co(tmd)(dien)Cl]ZnCl_4$ (assigned structure IIIb). This reflects the differing positions of the I-IIIb-(IIIa?) equilibrium, set up under basic conditions, and the relative solubility of the chloro tetrachlorozincate(II) salts. In both cases, the π and a-$[Co(AA)(dien)Cl]ZnCl_4$ isomers are relatively insoluble, whereas the *K* and especially d-$[Co(AA)(dien)Cl]ZnCl_4$ salts are more soluble.

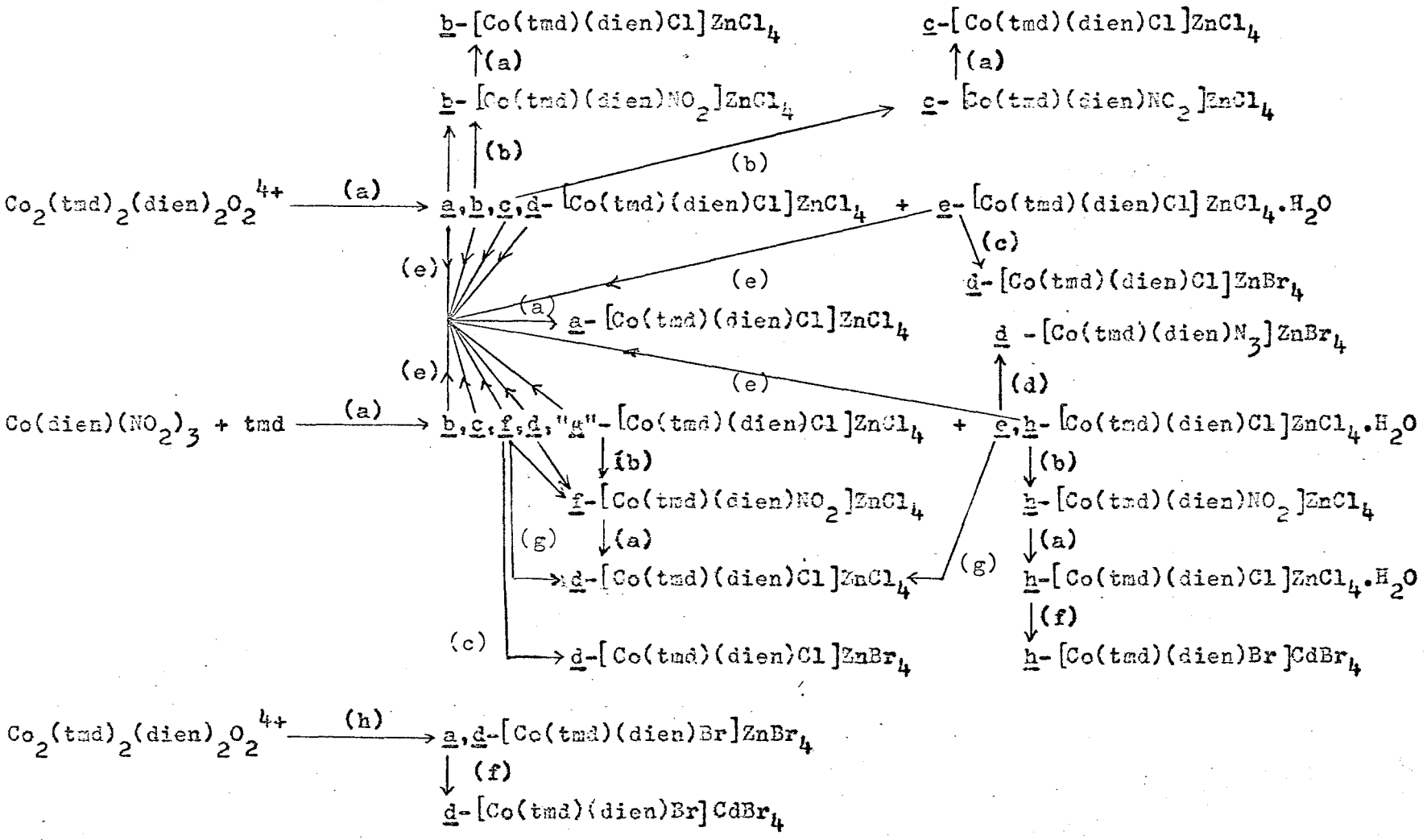


Figure 4.6 Isomeric and chemical interconversions in the $Co(tmd)(dien)X^{n+}$ system. Reagents: (a) = HCl(6-12 F) + $ZnCl_2$; (b) = HCl(0.1 F) + $NaNO_2$; (c) = HBr(6 F) + $ZnBr_2$ at room temp; (d) = NaN_3 then HBr (6 F) + $CdBr_2$ at room temp; (e) = NaOH (1 F); (f) = HBr (6F) + $CdBr_2$ at 100°; (g) heat at 120° for 12hr; (h) HBr (6 F) + $ZnBr_2$ at 80-90°.

The proposed or established configurations for the $[Co(tmd)(dien)Cl]ZnCl_4.xH_2O$ isomers are summarised in Table 4.18.

(2) N-methyl-1,3-propanediamine

Chemical Properties: Five isomers of $[Co(Me\text{-}tmd)(dien)Cl]ZnCl_4$ have been isolated and the visible absorption spectra (Fig. 3.17, 3.18 and 3.19) indicate that they are all distinguishable in aqueous acidic solution.

Interconversions between the isomers can be effected via (a) replacement of Cl^- by Br^-, when I-$[Co(Me\text{-}tmd)(dien)Cl]ZnCl_4$ gives III plus V-$[Co(Me\text{-}tmd)(dien)Br]CdBr_4$, and V-$[Co(Me\text{-}tmd)(dien)Cl]ZnCl_4$ gives V plus III-$[Co(Me\text{-}tmd)(dien)Br]CdBr_4$, and

(b) by base hydrolysis, when the isomerisations observed are II,IV → IV and I,III and V → V.

Conversion of the $[Co(Me\text{-}tmd)(dien)Cl]ZnCl_4$ isomers (I and V) to $[Co(Me\text{-}tmd)(dien)NO_2]ZnCl_4$ results in the isomerisation V → I. Decomposition of this nitro isomer (I) with HCl followed by the addition of $ZnCl_2$ gives I-$[Co(Me\text{-}tmd)(dien)Cl]ZnCl_4$ (i.e. retained configuration).

Replacement of coordinated chloride with azide (V isomer only) has been successful in this system.

Synthetic Methods: The partial reaction between trans-$Co(dien)(NO_2)_3$ and N-methyl-1,3-propanediamine, followed by treatment with $HCl/ZnCl_2$ gives only isomers IV and V. The isolation of the V isomer is perhaps surprising as the only nitro isomer obtained from this chloro isomer has the isomer I configuration. The isolation of this chloro isomer is probably facilitated by the relative insolubility of the $ZnCl_4^{2-}$ salt. This argument probably applies to the IV isomer also. The partial reaction observed is typical for N-substituted diamines and this has been mentioned before in the $[Co(Nip\text{-}ibn)(dien)Cl]ZnCl_4.xH_2O$ system.

Reaction of trans-$Co(dien)Cl_3$ with the diamine in aqueous solution forms all five known isomers in high yield. This reaction is more complete because the coordinated Cl^- ligands are readily lost in the basic conditions.

Only three (I, IV and V) of the chloro isomers were obtained as pure (less than 5-10% isomeric contamination) fractions at various stages of the synthetic methods (Tables 2.24 and 2.25). Careful fractional crystallisation of the $ZnCl_4^{2-}$ salts of mixtures containing high proportions of a particular isomer were also successful in purifying the major component. For example, fractional crystallisation of the I plus II mixture from fraction 4, crop 2, Table 2.24 gave the pure II isomer.

In all cases, the isomeric purity of any isolated fraction was monitored using the infrared spectrum. Each pure fraction was recrystallised twice from 3 F HCl containing $ZnCl_2$ before recording the characteristic infrared spectrum shown in Fig. 2.11 and 2.12.

Spectra: The visible absorption spectra of the $Co(Me\text{-}tmd)(dien)Cl^{2+}$ isomeric cations exhibit a well defined maxima at about 510 nm with prominent shoulders on this band. The V isomer also exhibits a well defined maxima at about 380 nm and this is just resolved in the IV isomer. Isomers I-III exhibit a shoulder on the side of the charge-transfer bands present in this region.

On comparison of the solution spectra of the $Co(AA)(dien)Cl^{2+}$ (AA = tmd, Me-tmd) systems, the IV,V and d isomers show the closest similarity, both in position and shape of the maxima. There is also a close correspondence of the I, II and III isomers with a and d-$Co(tmd)(dien)Cl^{2+}$.

Infrared spectra has been the method of distinguishing between these isomers. The characteristic bands used in the discrimination of the $[Co(Me\text{-}tmd)(dien)Cl]ZnCl_4$ are listed in Table 4.6.

Structural Assignments: Under the conditions of synthesis, only isomers of the type I, IIIa and IIIb would be expected to be formed, as the main synthetic reaction proceeds through a $Co(Me\text{-}tmd)(dien)OH^{2+}$ species. The ring

Table 4.6

Characteristic Infrared Frequencies (cm^{-1})

for $[Co(Me\text{-}tmd)(dien)Cl]ZnCl_4$ Isomers

I	II	III	IV	V
1601	1596	1593	1602	1602
1585	1585	1584	1575	1580
985	977	982	987	989
		974		
947	935	932	948	945
	927			
909		908	909	908
899	902	897	900	900
889			889	890
864	868	870	865	865
	845	845		
826	826	838	827	819
	806	811	821	

conformers isolated in the [Co(tmd)(dien)Cl]$ZnCl_4$ are not detected here, because each isomer isolated has a different visible absorption spectra (Fig. 3.17-3.19).

The five isomers can be divided into three groups, viz. I,II; III; IV,V and these are believed to correspond to the configurations IIIb, IIIa and I respectively.

The resolution of V-[Co(Me-tmd)(dien)Cl]$ZnCl_4$ (Fig. 3.35) assigns this isomer to structure I. To avoid confusion as to whether the above resolution is only of the asymmetric secondary nitrogen centre of the diamine, I-[Co(Me-tmd)(dien)Cl]$ZnCl_4$ (assigned to IIIb) was also resolved into its chiral components (Fig. 3.34). The ratio of the magnitudes of the peaks in the ORD spectra of these cations is about 13:1 and hence, only a relatively small part of the observed ORD spectra is due to the resolution of the coordinated asymmetric amine centre. Also, the magnitude of $[M]_{534}$ = -3363 deg.dm^{-1} ($\underline{M}$/100 cm^3)$^{-1}$ is of the order of that observed for (-)-$\underline{d}$-[Co(tmd)(dien)Cl]$ZnCl_4$ ($[M]_{507} \sim 4000^{o}$).

The assignment of the IV and I,II isomers to configurations I and IIIb respectively are based on their similarity with the known $\underline{d}$ and $\underline{a}$($\underline{b}$)-[Co(tmd)(dien)Cl]$ZnCl_4$ isomers. The visible absorption spectra (Fig. 3.18) of I and II - Co(Me-tmd)(dien)Cl^{2+} and $\underline{a}$($\underline{b}$)-Co(tmd)(dien)Cl^{2+}, in the 500 nm region, are similar, and that of IV-Co(Me-tmd)(dien)Cl^{2+}

is very similar to that of V-Co(Me-tmd)(dien)Cl^{2+} (Fig. 3.17).

The III isomer (tentatively assigned to structure IIIa) has only been isolated in small amounts. This would correspond to the small quantity of c-[Co(tmd)(dien)Cl]$ZnCl_4$ that has been synthesised. There is also a close correspondence in the III and c chloro isomers in their visible absorption spectra (Fig. 3.19).

The I, III, V and II,IV isomer groups are believed to be related by edgewise displacement or secondary amine proton inversion. The isolation of these two groups arises from the orientations in which the N-methyl-1,3-propanediamine ligand can coordinate (c.f. Co(pn)(dien)Cl^{2+}). However, the exact assignment is unknown.

In comparing the Co(AA)(dien)Cl^{2+} (AA - tmd,Me-tmd) systems, one notable difference is the configuration of the major product resulting from base hydrolysis, acidification and anation with $HCl/ZnCl_2$. All Co(tmd)(dien)Cl^{2+} isomers give a-[Co(tmd)(dien)Cl]$ZnCl_4$ (structure IIIb) while the Co(Me-tmd)(dien)Cl^{2+} isomers give IV or V-[Co(Me-tmd)(dien)Cl]$ZnCl_4$ (structure I). It is probable that the position of the equilibrium I-IIIb-(IIIa?) obtained under basic conditions is affected by N-substitution on the diamine, because the solubility of the five [Co(Me-tmd)(dien)Cl]$ZnCl_4$ isomers are similar.

The proposed configurations for the $[Co(Me\text{-}tmd)(dien)Cl]ZnCl_4$ isomers are summarised in Table 4.18.

(3) N-(n-butyl)-1,3-propanediamine

Chemical Properties: Two isomers of $[Co(Bu\text{-}tmd)(dien)Cl]ZnCl_4$ have been isolated and these are distinguishable in aqueous acidic solution (Fig. 3.20).

Interconversion between these isomers can be effected *via* replacement of Cl^- by Br^-, when VI-$[Co(Bu\text{-}tmd)(dien)Cl]ZnCl_4$ gives VII-$[Co(Bu\text{-}tmd)(dien)Br]CdBr_4$.

Replacement of coordinated chloride ligand with NO_2^- has been successful for the VI isomer. However, no isomerisations were detected in the formation and decomposition of this complex.

Synthetic Method: Both isomers have been prepared by the reaction of *trans*-$Co(dien)Cl_3$ with N-(n-butyl)-1,3-propanediamine, but the VII isomer is only detected in small amounts. The reaction is carried out in methanol containing sodium hydroxide as these appear to assist the formation of the $Co(Bu\text{-}tmd)(dien)OH^{2+}$ species. Both isomers were obtained as pure (less than 5-10% isomeric contamination) fractions at various stages of the synthetic methods. However, careful fractional crystallisation of the VI plus

VII mixture from fraction 2, crop 8, Table 2.27 gave the pure VII form.

The isomeric purity of the isolated fractions was monitored using the infrared spectrum. Each isomer was recrystallised twice from 2 F HCl containing $ZnCl_2$ before recording the characteristic infrared spectrum shown in Fig. 2.13.

Spectra: The visible absorption spectra of the $Co(Bu\text{-}tmd)(dien)Cl^{2+}$ isomeric cations exhibit two maxima at about 370 and 525 nm with prominent shoulders on the 525 nm band (Fig. 3.20). On comparison of the solution spectra of $Co(AA)(dien)Cl^{2+}$ (AA = tmd, Bu-tmd) systems, the VI, a(b) and VII, d pairs show close similarity.

Infrared spectra have been the method of distinguishing between the two isomers and the characteristic bands used in this discrimination are listed in Table 4.7.

Structural Assignments: In the $Co(Bu\text{-}tmd)(dien)Cl^{2+}$ system, the VI and VII isomers are believed to correspond to the configurations IIIb and I respectively. These assignments are based on the similarity of the visible absorption spectra with $Co(tmd)(dien)Cl^{2+}$ isomers as mentioned above. Also, only isomers of configurations I, IIIb and (IIIa?) should be formed in the synthetic route used because the synthesis involves the use of the $Co(Bu\text{-}tmd)(dien)OH^{2+}$ species. The two isomers isolated are related by edgewise displacement in the same way as the $Co(Nip\text{-}ibn)(dien)Cl^{2+}$ isomers are (1,2

Table 4.7

Characteristic Infrared Frequencies (cm^{-1})

of $[Co(Bu\text{-}tmd)(dien)Cl]ZnCl_4$ Isomers

VI	VII
1584	1600
1563	1569
968	
954	957
930	935
902	903
875	885
861	866
846	
818	823
785	790
770	760
721	743

Fig. 4.3). No ring conformation isomers have been detected for this system.

The proposed configurations for the $[Co(Bu\text{-}tmd)(dien)Cl]ZnCl_4$ isomers are summarised in Table 4. .

(4) N-cyclohexyl-1,3-propanediamine

Chemical Properties: Two isomers of $[Co(tmd\text{-}hex)(dien)Cl]ZnCl_4.xH_2O$ have been isolated and these are distinguishable in aqueous acidic solution indicating that these are not six-membered (Co-tmd) ring conformation isomers.

Synthetic Method: Both isomers have been prepared by the reaction of trans-$Co(dien)Cl_3$ with N-cyclohexyl-1,3-propanediamine. The reaction is carried out in methanol containing sodium hydroxide as these appear to assist the formation of the $Co(tmd\text{-}hex)(dien)OH^{2+}$ intermediate species and also the product tends to oil rather than crystallise from aqueous solution. Both isomers were obtained as pure (less than 5-10% isomeric contamination) at various stages in the synthetic method.

The isomeric purity of the isolated fractions was monitored using the infrared spectrum. Each isomer was recrystallised twice from 50% aqueous methanol containing 4 F HCl and $ZnCl_2$ before recording the characteristic infrared spectrum shown in Fig. 2.14.

Spectra: The visible absorption spectra of the $Co(tmd\text{-}hex)(dien)Cl^{2+}$ isomeric cations exhibit two well defined maxima at about 380 and 540 nm with prominent shoulders on the 540 nm band (Fig. 3.21). On comparison of the solution spectra of $Co(AA)(dien)Cl^{2+}$ (AA = tmd, tmd-hex) systems, the VIII, IX and d isomers show close similarity.

Infrared spectra have been the method of distinguishing between the two isomers and the characteristic bands used in this discrimination are listed in Table 4.8.

Structural Assignments: The VIII and IX isomers are believed to correspond to configuration I. This assignment is based on the similarity of the visible absorption spectra with $Co(tmd)(dien)Cl^{2+}$ isomers as mentioned above. The isomers must be interrelated by the different orientations of the unsymmetrical diamine ligand as illustrated in Fig. 4.3, the exact assignment being unknown. No ring conformation isomers have been detected for this system.

The proposed configurations for the $[Co(tmd\text{-}hex)(dien)Cl]ZnCl_4.xH_2O$ isomers are summarised in Table 4.18.

Table 4.8

Characteristic Infrared Frequencies (cm^{-1}) for

$[Co(tmd\text{-}hex)(dien)Cl]ZnCl_4.xH_2O$ Isomers

VIII	IX
	1609
1586	1588
1571	1576
1561	
1554	
956	943
935	927
923	917
	906
896	898
873	880
	866
844	845
820	821
797	790

(C) COMPLEXES OF 1,4-DIAMINES WITH DIETHYLENETRIAMINE

(1) 1,4-butanediamine

One isomer of $[Co(1,4\text{-bn})(dien)Cl]ZnCl_4$ has been isolated.

Synthetic Method: The isomer was prepared by the reaction, in50% aqueous methanol, of trans-$Co(dien)Cl_3$ and 1,4-butanediamine. The isomeric purity of each fraction was monitored using the infrared spectrum. However, no changes were observed in the spectra of the eight fractions isolated. The isomer (called 1) was recrystallised twice from 2 F HCl containing $ZnCl_2$ before recording the characteristic infrared spectrum shown in Fig. 2.15.

Spectra: The visible absorption spectrum of 1-$Co(1,4\text{-bn})(dien)Cl^{2+}$ exhibits two well defined maxima at 371 and 523 nm with a prominent shoulder on the 523 nm band (Fig. 3.22). On comparison of the solution spectra of $Co(AA)(dien)Cl^{2+}$ (AA = en, tmd, 1,4-bn) the π, d and 1 isomers show very close similarity (Table 4.9).

The characteristic infrared bands of 1-$[Co(1,4\text{-bn})(dien)Cl]ZnCl_4$ are listed in Table 4.10.

Structural Assignment: This isomer is believed to correspond to configuration I (Fig. 4.18) because of the similarity of the visible absorption spectra mentioned above, but the assignment is very tentative at this stage.

Table 4.9

Visible Absorption Maxima and Minima for π-Co(en)(dien)Cl^{2+}, d-Co(tmd)(dien)Cl^{2+} and 1-Co(1,4-bn)(dien)Cl^{2+} in Aqueous Solution at 20-25° [a]

Complex	λmin	λmax	λmin	λmax	λmin	λmax
1-Co(1,4-bn)(dien)Cl^{2+}	334	371	426	481sh[b]		523
d-Co(tmd)(dien)Cl^{2+}	329	369	424	470sh		535
π-Co(en)(dien)Cl^{2+}	326	362	415	475sh		525

a Wavelengths are in nanometers

b sh = shoulder

Table 4.10

Characteristic Infrared Frequencies (cm^{-1}) of

1 - $[Co(1,4\text{-bn})(dien)Cl]ZnCl_4$

1599	923	771
1571	902	741
996	887	683
980	848	662
963	795	580

General Observations in $Co(AA)(dien)X^{n+}$ Complexes

(a) Synthetic Routes: (i) The reaction of trans-$Co(dien)(NO_2)_3$ with diamines produces cis-dien complexes as the major products. Thus, extensive trans → cis isomerisation is involved in this reaction. The yields are high and the method is the most efficient for synthesising isomers of configuration II, e.g. H-$[Co(pn)(dien)Cl]ZnCl_4.2H_2O$.

(ii) The reaction of trans-$Co(dien)Cl_3$ produces configuration I, IIIb and IIIa isomers only, in high yield. The formation of $Co(AA)(dien)OH^{2+}$ species appears to prevent the isolation of isomers of configuration II from this synthesis.

(iii) The reaction of μ-peroxo dicobalt(III) decaamine perchlorates with $HCl/ZnCl_2$ produces configuration I and IIIb isomers in a medium yield (ca. 35%). Configurations II and IIIa have been isolated in small quantities for some systems.

(b) Visible Absorption Spectra: From the data presented in Table 4.11, it can be seen that the position of the absorption maxima (and minima) gradually progresses to larger wavelengths as

(i) the ring size of the coordinated diamine increases,

(ii) the amount of C-substitution on the 1,2-diamine increases,

(iii) the amount of N-substitution of the 1,3-diamine increases.

Table 4.11

Visible Absorption Maxima and Minima for

$Co(AA)(dien)Cl^{2+}$ Structure I Cations [a]

(AA = en, pn, ibn, Nip-ibn, stien, tmd,

Me-tmd, Bu-tmd, tmd-hex, 1,4-bn)

Complex	λmin	λmax	λmin	λmax	λmin	λmax
π-Co(en)(dien)Cl^{2+}	334	362	415	481sh[b]		525
A-Co(pn)(dien)Cl^{2+}	327	368	417	483sh		518
O-Co(ibn)(dien)Cl^{2+}	332	367	418	489		530sh
XI-Co(Nip-ibn)(dien)Cl^{2+}	342	375	429	495sh		546
o-Co(stien)(dien)Cl^{2+}	350	365	426	470sh		534
d-Co(tmd)(dien)Cl^{2+}	329	369	424	470sh		535
V-Co(Me-tmd)(dien)Cl^{2+}	337	379	434	505sh		546
VII-Co(Bu-tmd)(dien)Cl^{2+}	346	377	435	485sh		545
IX-Co(tmd-hex)(dien)Cl^{2+}	353	382	440	495sh		550
1-Co(1,4-bn)(dien)Cl^{2+}	334	371	426	481sh		523

a Wavelengths are in nanometers

b sh = shoulder

The results obtained in (i) parallel those of the trans-triacido(triamine)cobalt(III) complexes studied in Chapter 1.

(c) Products of Base Hydrolysis: The products of base hydrolysis are mixtures of isomers of configurations I and IIIb. The amount of each configuration formed appears to depend on (i) ring size of diamine

(ii) solubility of isomers I and IIIb within each particular system.

(d) O.R.D. Spectra: The magnitude of molar rotations increases with increase in the ring size of the diamine ligand. This is in agreement with the observations of Woldbye[92].

(D) COMPLEXES OF 1,2-DIAMINES WITH 1,4,8-TRIAZAOCTANE

(1) Ethylenediamine

Two isomers of $[Co(2,3\text{-tri})(en)Cl]ZnCl_4$ have been isolated and the visible absorption spectra of these indicate that they are distinguishable in aqueous acidic solution (Fig. 3.23). In addition to these isomers, constant composition mixtures "ρ", "*i*" and "Δ" have also been formed.

Interconversions between the two isomers can be effected via base hydrolysis, when

η-[Co(2,3-tri)(en)Cl]$ZnCl_4$ gives Σ-[Co(2,3-tri)(en)Cl]$ZnCl_4$, and by replacement of Cl^- by I^- when Σ-[Co(2,3-tri)(en)Cl]$ZnCl_4$ gives η-[Co(2,3-tri)(en)I]$ZnCl_4$.

Conversion of the [Co(2,3-tri)(en)Cl]$ZnCl_4$ isomers to [Co(2,3-tri)(en)NO_2]$ZnCl_4$ also results in isomerisation. Thus, the η chloro complex gives a mixture of the η and Σ nitro isomers. Decomposition of the η and Σ nitro isomers with HCl followed by the addition of $ZnCl_2$ gives chloro products with retained configuration.

Synthetic Methods: The amount of any particular [Co(2,3-tri)(en)Cl]$ZnCl_4$ isomer produced is not dependent upon the method of synthesis used. Thus the synthetic routes used produce approximately equal proportions of the two isomers.

Both isomers were obtained as pure (less than 5-10% isomeric contamination) fractions at various stages of the synthetic methods (Tables 2.32-2.34). Careful fractional crystallisation of the $ZnCl_4^{2-}$ salts of mixtures containing high proportions of one of the isomers were also successful in purifying the major component. The "ρ", "*i*" and "Δ" isomers, although depositing as constant crystallising phases, have the following composition (Table 3.1):

"ρ" = 69%
η-[Co(2,3-tri)(en)Cl]$ZnCl_4$ plus 31%
η-[Co(2,3-tri)(en) NO_2]$ZnCl_4$, "*i*" = 63%

Σ-[Co(2,3-tri)(en)Cl]$ZnCl_4$ plus 37%

Σ-[Co(2,3-tri)(en)NO_2]$ZnCl_4$ and "Δ" = 14%

η-[Co(2,3-tri)(en)Cl]$ZnCl_4$ plus 14%

Σ-[Co(2,3-tri)(en)Cl]$ZnCl_4$ plus 72%

Σ-[Co(2,3-tri)(en)NO_2]$ZnCl_4$.

In all cases, the isomeric purity of any particular isolated fraction was monitored using the infrared spectrum. Each pure fraction was recrystallised twice from 2.5 F HCl containing $ZnCl_2$ before recording the characteristic infrared spectrum shown in Fig. 2.16.

Spectra: The visible absorption spectra (Fig. 3.23) of the Co(2,3-tri)(en)Cl^{2+} isomeric cations exhibit two well defined maxima at about 365 and 540 nm with prominent shoulders on the short wavelength side of the 540 nm band. The intensities of these bands (Table 3.1) are similar to those of the isomers of Co(en)(dien)Cl^{2+} and are typical of d-d transitions in an octahedral Co(III) complex with a CoN_5Cl chromophore. The positions of the maxima (and minima) are intermediate between those observed for Co(en)(dien)Cl^{2+} (*K* isomer) and Co(en)(dpt)Cl^{2+} (α and β isomers)[30], thus paralleling the results for the Co(ABA)X_3 systems obtained in Chapter 1.

Infrared spectra have been the main method of distinguishing between the two isomers and the characteristic bands used in this discrimination are listed in Table 4.12.

Table 4.12

Characteristic Infrared Frequencies (cm^{-1})

of $[Co(2,3\text{-tri})(en)Cl]ZnCl_4$ Isomers

η	Σ
1609	
1598	
1584	1586
1567	1575
962	964
940	938
901	905
892	894
886	
877	877
868	869
824	823

The NMR spectra of the two isomers are presented in Fig. 3.38 and they are similar to that obtained for *K*-[Co(en)(dien)Cl]$ZnCl_4$ (E, Fig. 3.37) and α and β-[Co(en)(dpt)Cl]$ZnCl_4$ (A and D, Fig. 3.36). In particular the 6.8 ppm signal of η-[Co(2,3-tri)(en)Cl]$ZnCl_4$ is intermediate between that of *K*-[Co(en)(dien)Cl]$ZnCl_4$ (7.9 ppm) and β-[Co(en)(dpt)Cl]$ZnCl_4$ (5.9 ppm). The position of this signal appears to be dependent on the size of the chelate rings within these complexes.

Structural Assignments: There are potentially four geometric isomers possible for the Co(en)(2,3-tri)Cl^{n+} system (I, II, IIIa and IIIb) but within these a variety of conformational isomers can be postulated.

For a complex containing a peripheral tridentate ligand there exists the possibility of the IIIa, IIIb structures related by NH(triamine) proton inversion. However, this is not possible for facial isomers (e.g. I) in the diethylenetriamine system, but with the more flexible 1,4,8-triazaoctane ligand, the NH proton can again adopt alternative position. Models of the isomers of Co(en)(2,3-tri)Cl^{2+} in the facial configuration show that these forms are significantly strained, and thus are unlikely to be stable.

In addition to the isomerisation due to NH proton inversion, there exists the possibility of a variety of ring conformations within the six-membered ring of the

1,4,8-triazaoctane ligand.

If only chair and twist boat six-membered ring conformations are considered, there are two possible configurations for isomers IIIa and IIIb, and three for isomers I or II.

In addition, each configuration is potentially optically active because the 1,4,8-triazaoctane ligand contains an asymmetric secondary amine centre.

However, it appears that no ring conformation isomers have been isolated for $[Co(2,3\text{-tri})(en)Cl]ZnCl_4$ because the two isomers obtained are distinguishable in aqueous acidic solution. Also, since only two isomers have been isolated, it is probable that some of the basic configurations I-IIIb are not formed from these synthetic routes, or the 'missing' isomers are too soluble to be isolated. This is supported by the observation that only two isomers are formed in the $Co(en)(dpt)Cl^{2+}$ system[30], and both have been shown to have a peripheral (or <u>trans</u>) dpt configuration (IIIa, IIIb)[33-34]. The only reported complex of 1,4,8-triazaoctane in a <u>cis</u> configuration is $Co(2,3\text{-tri})(OH_2)_3^{3+}$ [59a].

In this system the Σ and η are believed to correspond to the configurations IIIa and IIIb, respectively. The six-membered ring probably adopts a chair configuration and models show that this conformation is less strained than the twist-boat form.

The assignments of these isomers are based on their similarity with the known α (IIIa)[34] and β (IIIb)-$[Co(en)(dpt)Cl]ZnCl_4$[33] isomers, especially in their visible absorption and NMR spectra. Chemical evidence supports this assignment, as the η isomer isomerises to the Σ isomer under base hydrolysis and a β to α-$Co(en)(dpt)Cl^{2+}$ is similarly effected. Also the Σ:α and η:β-$[Co(ABA)(en)NO_2]ZnCl_4$ (ABA = 2,3-tri,dpt respectively) isomer pairs have similar (low and moderate, respectively) solubility in acetone/2-propanol solution. Also, by monitoring the change in colour of solutions of these complexes in water at pH 7 indicates that the isomers have similar rates of base hydrolysis.

The proposed configurations for the $[Co(en)(2,3\text{-tri})Cl]ZnCl_4$ isomers are summarised in Table 4.18.

(E) COMPLEXES OF 1,2-DIAMINES WITH DIPROPYLENETRIAMINE

(1) Ethylenediamine

Two isomers of $[Co(en)(dpt)Cl]ZnCl_4$ have been isolated[30] and the crystal structures of α-$[Co(en)(dpt)Cl]I_2.H_2O$[34] and β-$[Co(en)(dpt)Cl]ZnCl_4$[33] have been reported[32].

For complexes containing the trans dpt configuration, the NH proton on the secondary coordinated secondary amine

group can be either adjacent to (IIIa)[34] or remote from (IIIb)[33] the coordinated acido group. This situation is also possible for this ligand in the facial configuration (I and II), this point not being clear in reference 30. All structural determinations of complexes containing dpt as a ligand show the triamine in the trans configuration and dpt complexes in a facial configuration have not yet been established[59a].

In addition to the isomerisation due to NH proton orientation, there exists the possibility of a variety of ring conformations within the six-membered rings. The existence of these has been reviewed earlier in the $Co(tmd)(dien)Cl^{2+}$ system. Both chair-chair (as in $[Ni(dpt)_2](ClO_4)_2$[90]) and chair-twist-boat (as in α-$[Co(en)(dpt)Cl]I_2.H_2O$[34] and β-$[Co(en)(dpt)Cl]ZnCl_4$[33]) configurations have been observed and in the oxalate bridged trigonal bipyramid $[Zn_2(dpt)_2OX](ClO_4)_2$ complex[91], the dpt ligands are not equivalent, one being chair-chair and the other chair-twist-boat. However, no isomers due solely to the ring conformations have been reported.

In view of the absence of cis-dpt complexes, the synthesis of $[Co(en)(dpt)Cl]ZnCl_4$ isomers using trans-$Co(dpt)(NO_2)_3$[60] as the starting material was attempted. This material was used because reaction of the structurally related trans-$Co(dien)(NO_2)_3$ with diamines produces cis

isomers as the major products. However, the products isolated from the synthesis (Table 2.37) were the α and β isomers described above. Hence, cis complexes containing the dpt ligand have not been isolated and this can be explained by (i) the complexes being too soluble to be isolated by the crystallisation procedures used or

(ii) a rapid and irreversible isomerisation of cis to trans configurations during the synthesis.

(2) 1,2-propanediamine

Four isomers of $[Co(pn)(dpt)Cl]ZnCl_4$ have been isolated and the visible absorption spectra indicate that they are all distinguishable in aqueous acidic solution.

Interconversions between the isomers can be effected via replacement of Cl^- by Br^- when the partial isomerisations J → J+M and K → L+K occur, or by base hydrolysis, where K gives L and M gives J only.

Conversion of $[Co(pn)(dpt)Cl]ZnCl_4$ isomers to $[Co(pn)(dpt)NO_2]ZnCl_4$ results in extensive isomerism. Thus the K and M isomers give only the K and M nitro forms, while the J and L isomers give mixtures of the J,M and L,K nitro complexes respectively. Decomposition of the nitro isomers with HCl followed by the addition of $ZnCl_2$ gives chloro products with retained configuration.

Synthetic Methods: The reaction between trans-$Co(dpt)(NO_2)_3$ and 1,2-propanediamine followed by treatment with $HCl/ZnCl_2$

gives the K and M isomers and the L isomer as a minor component. This is perhaps surprising as the J, K, L and M nitro isomers have been prepared by reacting the chloro isomers with nitrite ion. Each of these would be expected to be present in this synthetic reaction.

Decomposition of $Co_2(pn)_2(dpt)_2O_2^{4+}$ in HCl containing $ZnCl_2$ results in the formation of all four isomers.

All of the $[Co(pn)(dpt)Cl]ZnCl_4$ isomers were obtained as pure (less than 5-10% isomeric contamination)fractions at various stages of the synthetic methods (Tables 2.38, 2.39). Careful fractional crystallisation of the $ZnCl_4^{2-}$ salts of mixtures containing high proportions of a particular isomer were also successful in purifying the major component. For example, fractional crystallisation of the K plus M mixture from crop 9, Table 2.38 gave the pure M form.

In all cases, the isomeric purity of any isolated fraction was monitored using the infrared spectrum. Each pure isomer was recrystallised twice from 2 F HCl containing $ZnCl_2$ before recording the characteristic infrared spectrum shown in Fig. 2.17.

Spectra: The visible absorption spectra of the $Co(pn)(dpt)Cl^{2+}$ isomeric cations exhibit two well defined maxima at about 375 and 550nm with prominent shoulders on the low wavelength side of the 550 nm band (Fig. 3.24 and

3.25). On comparison of the solution spectra in the $Co(AA)(dpt)Cl^{2+}$ (AA = en,pn) systems, the α and J,L isomers show close similarity especially in the position of the ca. 550 nm band, and the β and K,M isomers also show a close similarity.

Infrared spectra have been the main method of distinguishing between these isomers and the characteristic bands used in this discrimination are listed in Table 4.13.

Structural Assignments: It is probable that in the $Co(pn)(dpt)Cl^{2+}$ system the J,L and K,M isomers correspond to the α and β-$Co(en)(dpt)Cl^{2+}$ cations respectively (i.e. to structures IIIa and IIIb) and by analogy with the α and β-$Co(en)(dpt)Cl^{2+}$ cations, the $Co(pn)(dpt)Cl^{2+}$ isomers are believed to have the chair-twist-boat dpt configurations.

The assignment of these isomers is based on a comparison with the visible absorption spectra of α and β-$Co(en)(dpt)Cl^{2+}$ [30] (Table 3.1). Chemical evidence supports this assignment and the products of base hydrolysis of the K and M isomers are the L and J isomers respectively. Also, the L,J;α and K,M;β-$[Co(AA)(dpt)NO_2]ZnCl_4$ (AA = pn,en respectively) isomer pairs have similar (low and moderate, respectively) solubility in acetone/2-propanol solution.

From the reactions described above, it is believed that the L, K and J, M isomers are related by proton inversion at the secondary amine of the dpt ligand. The isolation of

Table 4.13

Characteristic Infrared Frequencies (cm^{-1}) of

$[Co(pn)(dpt)Cl]ZnCl_4$ Isomers

J	K	L	M
1606	1623	1626	
1588	1596	1586	1599
1576	1582		1582
1567	1577		1579
	1563		1565
	984	989	988
964	962		965
			960
946	937	937	940
925	928	927	927
910	911		909
	902	900	
895	883	886	885
873	867		
846	848	837	850
806	822	822	821

isomer pairs, i.e. L,K corresponding to α-[Co(en)(dpt)Cl] $ZnCl_4$ arises from the two orientations in which the 1,2-propanediamine ligand can coordinate (Fig. 4.2). However, the exact assignment of these isomers is not known but determination of the structure of one of the isomers will automatically assign the structures of the remaining three.

The proposed configurations for the [Co(pn)(dpt)Cl] $ZnCl_4$ isomers are summarised in Table 4.18.

(3) Isobutylenediamine

Four isomers of $[Co(ibn)(dpt)Cl]ZnCl_4.xH_2O$ [w, x, y (monohydrate), z] have been isolated and the visible absorption spectra indicate that they are all distinguishable in aqueous acidic solution. Although the y form is a monohydrate, it appears to be a separate isomer rather than a hydrated form of another isomer. Thus, the y form yields only itself on recrystallisation from aqueous HCl containing $ZnCl_2$.

Interconversion between the isomers can be effected via base hydrolysis when the x and y chloro isomers give the w and z chloro isomers, respectively.

Conversion of these isomers to $Co(ibn)(dpt)NO_2^{2+}$ and decomposition in situ with HCl followed by the addition of $ZnCl_2$ results in partial conversion of the w, z isomers to the x, y isomers respectively.

Synthetic Methods: The reaction between trans-$Co(dpt)Cl_3$[60] and isobutylenediamine, followed by treatment with $HCl/ZnCl_2$ gives all four isomers in a moderate yield (ca. 21%).

Decomposition of $Co_2(ibn)_2(dpt)_2O_2^{4+}$ in HCl containing $ZnCl_2$ forms only the w, x and z isomers in a very low yield.

All of the isomers were obtained as pure (less than 5-10% isomeric contamination) fractions at various stages of the synthetic methods (Tables 2,42, 2,43). Careful fractional crystallisation of the $ZnCl_4^{2-}$ salts of mixtures containing high proportions of a particular isomer were also successful in purifying the major component. For example, fractional crystallisation of the y plus x mixture from fraction 1, crop 8, Table 2.43 gave the pure y isomer. Each pure fraction was recrystallised twice from 4 F HCl containing $ZnCl_2$ before recording the characteristic infrared spectrum shown in Fig. 2.18.

Spectra: The visible absorption spectra (Fig. 2.26, 2.27) of the $Co(ibn)(dpt)Cl^{2+}$ isomeric cations exhibit two well defined maxima at about 375 and 560 nm with prominent shoulders on the short wavelength side of the 560 nm band. On comparison of the solution spectra of the $Co(AA)(dpt)Cl^{2+}$ (AA = ibn,en) systems, the α and w,z isomers show a close similarity both in the position of the maxima and the intensities (Table 3.1). There is also a close correspondence with the x, y isomers with

β-$Co(en)(dpt)Cl^{2+}$.

Infrared spectra have been the main method of distinguishing between these isomers and the characteristic bands used in this discrimination are listed in Table 4.14.

Structural Assignments: It is probable that the w, z and x, y isomers correspond to the α and β-$[Co(en)(dpt)Cl]ZnCl_4$[30] isomers (i.e. structures IIIa and IIIb) respectively. By analogy with the above isomers, the $[Co(ibn)(dpt)Cl]ZnCl_4.xH_2O$ isomers are believed to have the chair-twist-boat dpt configuration.

The assignment of the w, z and x, y isomers to the IIIa and IIIb structure, respectively, is based on the comparison with the visible absorption spectra of α and β-$Co(en)(dpt)Cl^{2+}$, as already described. Chemical evidence supports this assignment, as the x and y forms isomerise to the w and z forms respectively under base hydrolysis and a β to α-$Co(en)(dpt)Cl^{2+}$ isomerisation is similarly effected. Also there is a partial isomerisation of the w and z isomers to the x and y isomers on treatment with NO_2^-.

The w, x and z, y isomer pairs are believed to be related by proton inversion at the secondary amine of the dpt ligand and these isomers show similar properties to those of $[Co(pn)(dpt)Cl]ZnCl_4$, as already described. Thus the two sets of isomer pairs are believed to be related by the orientation of the coordinated isobutylenediamine ligand,

Table 4.14

Characteristic Infrared Frequencies (cm^{-1}) for

$[Co(ibn)(dpt)Cl]ZnCl_4 \cdot xH_2O$ Isomers

w (x=0)	x (x=0)	y (x=1)	z (x=0)
		1625	1626
1605	1605	1621	1620
1597	1593	1587	1593
1581			
1574	1575		1569
			996
987	988	988	987
967	962	972	968
		962	
937	944	943	934
926	925	932	919
		912	906
897	893	898	900
	887	885	884
	870		
	824	837	823
817	814	815	808

the exact assignment being unknown (Fig. 4.2).

The proposed configurations for the $[Co(ibn)(dpt)Cl]ZnCl_4.xH_2O$ isomers are summarised in Table 4.18.

(4) Meso-stilbenediamine:

Four isomers of $[Co(stien)(dpt)Cl]ZnCl_4$ have been isolated and the visible absorption spectra indicate that these are distinguishable in aqueous acidic solution. Synthetic Method: The reaction of trans-$Co(dpt)Cl_3$[60] with meso-stilbenediamine produces all four isomers in high yield. All of the isomers were obtained as pure (less than 5-10% isomeric contamination) fractions at various stages in the synthesis. The isomeric purity of any isolated fraction was monitored using the infrared spectrum. Each pure fraction was recrystallised twice from 50% aqueous methanol by the addition of 6 F HCl containing $ZnCl_2$ before recording the characteristic infrared spectrum shown in Fig. 2.19. Spectra: The visible absorption spectra of the $Co(stien)(dpt)Cl^{2+}$ isomeric cations exhibit a well defined maxima at about 545 nm with prominent shoulders on this band. Each isomer exhibits a shoulder in the charge transfer band at about 370 nm (Fig. 3.28, 3.29). These spectra show some similarity with the α and β-$Co(en)(dpt)Cl^{2+}$ analogs and thus the s, t and u, v isomer pairs are probably

structures IIIa and IIIb, respectively.

The characteristic bands used in the discrimination of these isomers are listed in Table 4.15.

Structural Assignments: As mentioned above, the s, t and u, v isomer pairs are probably of structures IIIa and IIIb respectively. The modifications of these structures have already been described in the $[Co(stien)(dien)Cl]ZnCl_4$ system (Fig. 4.4) and it appears that all of these forms have been isolated for this system. However, the exact assignment of these structural modifications is unknown.

The proposed configurations for the $[Co(stien)(dpt)Cl]ZnCl_4$ isomers are summarised in Table 4.18.

(F) COMPLEXES OF 1,3-DIAMINES WITH DIPROPYLENETRIAMINE

(1) 1,3-propanediamine

Six infrared distinguishable forms of $[Co(tmd)(dpt)Cl]ZnCl_4.xH_2O$ [i (x=0), j (x=2), k (x=1), l (x=1), m (x=2), n (x=1)] have been isolated by various synthetic routes but the visible absorption spectra indicate that only two groups, viz i, j, m, n; k, l are distinguishable in solution. The j (x=2), m (x=2) and n (x=1) forms are unstable at room temperature, completely and irreversibly converting to the anhydrous i isomer

Table 4.15

Characteristic Infrared Frequencies (cm^{-1}) for

$[Co(stien)(dpt)Cl]ZnCl_4$ Isomers

s	t	u	v
		1618	
1605	1603	1604	1606
1574	1573		1579
	1563	1565	1570
		1560	
805	802		
788	791	794	787
756	754	758	761
748	736	745	750
715	713	712	735
696	694	704	698

after a period of 6 months, 1 day and three weeks respectively. Heating these complexes in the solid state at 70° for 12 hours results in the complete conversion to the anhydrous i form.

The isolation of the unstable forms is apparently facilitated by the relative insolubility of the $ZnCl_4^{2-}$ salts, the order of solubility being m < i ~ j < n < l ~ k. The relatively soluble k and l isomers are both thermally stable.

Interconversions between the two sets of isomers (i, j, m, n) and (k, l) can be effected via replacement of Cl^- by Br^-, when i-$[Co(tmd)(dpt)Cl]ZnCl_4$ gives k-$[Co(tmd)(dpt)Br]ZnBr_4.H_2O$, or by base hydrolysis (where k gives i). In fact, on reaction with base and acidification and anation with $HCl/ZnCl_2$, all isomeric forms of $[Co(tmd)(dpt)Cl]ZnCl_4.xH_2O$ give the i isomer (Fig. 4.8).

Conversion of the $[Co(tmd)(dpt)Cl]ZnCl_4.xH_2O$ isomers to $[Co(tmd)(dpt)NO_2]ZnCl_4$ results in extensive isomerism. Thus, the chloro pairs i, j and k, l give the i and l nitro products, respectively. Decomposition of the i and l nitro isomers with HCl followed by the addition of $ZnCl_2$ gives the i chloro isomer only.

Replacement of coordinated chloride ligand with iodide or thiocyanate has not been successful in these systems. With iodide there is extensive formation of Co^{2+} and I_2 and

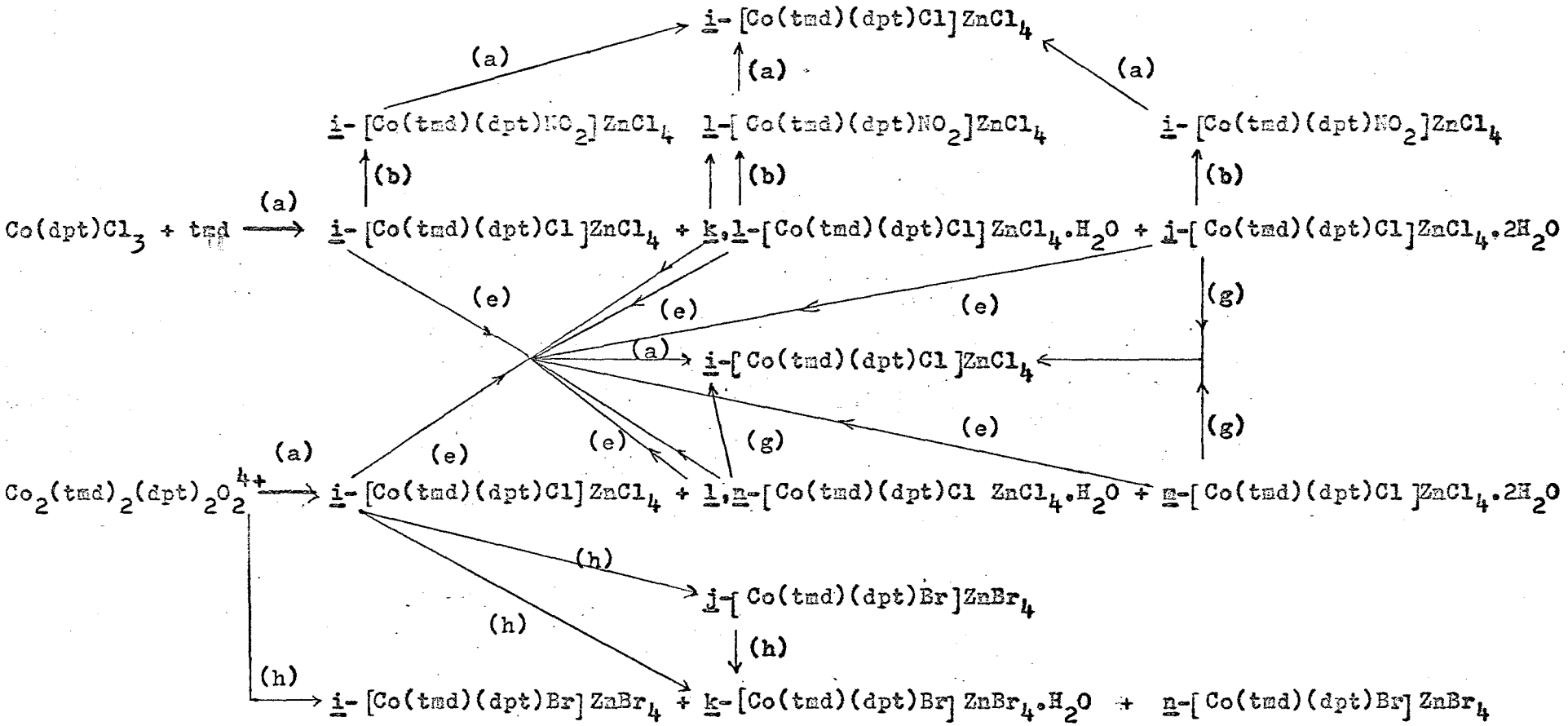


Figure 4.8 Isomeric and chemical interconversions in the $Co(tmd)(dpt)X^{n+}$ system. Reagents: (a) = HCl (6-12 F) + $ZnCl_2$; (b) = HCl (0.1 F) + $NaNO_2$; (c) = HBr (6 F) + $ZnBr_2$ at room temp.; (d) = NaN_3 then HBr (6 F) + $CdBr_2$ at room temp.; (e) = NaOH (1 F); (f) = HBr (6 F) + $CdBr_2$ at 100°; (g) = heat at 120° for 12 hr; (h) HBr (6 F) + $ZnBr_2$ at 80-90°.

with thiocyanate, trans-$Co(dpt)(NCS)_3$ is the only identifiable product.

Synthetic Methods: The amount of any particular $[Co(tmd)(dpt)Cl]ZnCl_4.xH_2O$ isomer produced is markedly dependent upon the method of synthesis used. The reaction between trans-$Co(dpt)(NO_2)_3$[60] and 1,3-propanediamine, followed by treatment with $HCl/ZnCl_2$ gives no pentaamine products, in agreement with Schlessinger[28].

Decomposition of $Co_2(tmd)_2(dpt)_2O_2^{4+}$ in HCl containing $ZnCl_2$ forms the i, l, m and n isomers, the i isomer being a very minor component.

Reaction of trans-$Co(dpt)Cl_3$[60] with 1,3-propanediamine in aqueous solution, followed by the addition of $HCl/ZnCl_2$ gives low yields (26% total) of the k and l isomers, the major product being trans-$[Co(tmd)_2Cl_2]Cl$. This is again similar to the results reported by Schlessinger[28], but he was unable to detect any chloro pentaamine product.

All of the $[Co(tmd)(dpt)Cl]ZnCl_4.xH_2O$ isomers were obtained as pure (less than 5-10% isomeric contamination) fractions at various stages of the synthetic methods. Careful fractional crystallisation of the $ZnCl_4^{2-}$ salts of mixtures containing high proportions of a particular isomer were also successful in purifying the major component. For example, fractional crystallisation of the k plus l mixture from crop 7, Table 2.47 gave the pure k form.

In all cases, the isomeric purity of any isolated fraction was monitored using the infrared spectrum. Each pure isomer was recrystallised twice from 2 F HCl containing $ZnCl_2$ before recording the characteristic infrared spectrum shown in Fig. 2.20 and 2.21.

Spectra: The visible absorption spectra of the $Co(tmd)(dpt)Cl^{2+}$ isomeric cations exhibit two well defined maxima at about 370 and 520 nm with prominent shoulders on the long wavelength side of the 520 nm band (Fig. 3.30).

It has previously been mentioned that the six solid state isomers of $[Co(tmd)(dpt)Cl]ZnCl_4.xH_2O$ can be divided into two groups i, j, m, n; k, l with distinguishable solution spectra. From the solution spectra of the $Co(AA)(dpt)Cl^{2+}$ isomers (AA = tmd, en), the i, j, m, n group and α[30,33] appear to be similar in the relative positions of the maxima to the k, l and β[30,34] isomers.

Infrared spectra have been the main method of distinguishing between the solid state isomers. The characteristic bands used in the discrimination of these isomers are listed in Table 4.16.

Structural Assignments: In addition to the isomerisation due to secondary amine proton inversion, there exists the possibility of a variety of ring conformations. Other systems containing ring conformations have already been discussed. It is probable that in the $Co(tmd)(dpt)Cl^{2+}$

Table 4.16

Characteristic Infrared Frequencies (cm^{-1}) for

$[Co(tmd)(dpt)Cl]ZnCl_4 \cdot xH_2O$ Isomers

i (x=0)	j (x=2)	k (x=1)	l (x=1)	m (x=2)	n (x=1)
	1622	1632		1616	1618
1601	1618		1601	1600	1602
1592		1594	1587	1591	1590
1577	1570	1578	1570	1572	1571
				1101	1100
				1060	1008
986	944	981	984	983	982
969	959	964	959	970	970
930	932	942	939	931	933
910	908	931	926	913	910
894	889	901	900	894	892
885	882	892	885	886	887
822	826	814	820	822	825
			813		

system, the two groups of solid state isomers that give different visible absorption spectra in solution, namely, i, j, m, n and k, l correspond to the α and β-Co(en)(dpt)Cl^{2+} cations (structures IIIa and IIIb) respectively, and that the thermally unstable solid state isomers are due to different ring conformations.

If only chair and twist-boat six-membered ring conformations are considered, there are 16 possible configurations for each of the structures IIIa and IIIb. If the dpt rings in IIIa or IIIb are labelled R_1 and R_2 and the tmd ring R_3, then the 8 combinations, in the order R_1, R_2, R_3 are: c, c, c; tb, c, c; c, tb, c; tb, c, tb; c, tb, tb; tb, tb, tb; tb, tb, c; c, c, tb (c = chair, tb = twist-boat). The basic set of 8 configurations is doubled because the tmd ring can lie either above or below the plane defined by the Co, Cl and NH(dpt) groups (Fig. 4.7).

By analogy with the α and β-Co(en)(dpt)Cl^{2+} and trans-$Co(tmd)_2Cl_2^+$ cations, the stable i and k, l forms of Co(tmd)(dpt)Cl^{2+} are believed to have the chair-twist-boat dpt and chair tmd configurations, but the conformations within the thermally unstable j, m and n isomers cannot be assigned. The two thermally stable k and l isomers, with identical visible absorption spectra, are believed to have configuration IIIb with a chair-twist-boat dpt system and a chair tmd ring either above or below the plane of the Co, Cl

and NH(dpt) groups (Fig. 4.7), the exact assignment being unknown.

The assignment of the i (and of the j, m, n isomers which revert to it) and k, l forms to the IIIa and IIIb structures, respectively, is based on a comparison with the visible absorption spectra of α and β-$Co(en)(dpt)Cl^{2+}$ (see Table 3.1 and compare Fig. 3.30 with Fig. 2 reference 30). Chemical evidence supports this assignment, as the k, l forms isomerise to the i form under base hydrolysis and a β to α-$Co(en)(dpt)Cl^{2+}$ isomerisation is similarly effected. Also, the i; α and l; β-$[Co(AA)(dpt)NO_2]ZnCl_4$ (AA = tmd, en respectively) isomer pairs have similar (low and moderate, respectively) solubility in acetone/2-propanol solution.

The proposed configurations for the $[Co(tmd)(dpt)Cl]ZnCl_4.xH_2O$ isomers are summarised in Table 4.18.

Table 4.17

Visible Absorption Maxima and Minima for $Co(AA)(dpt)Cl^{2+}$ Structure IIIb Cations. [a]

(AA = en, pn, ibn, stien, tmd)

Complex	λ min	λ max	λ min	λmax	λ min	λ max
β-$Co(en)(dpt)Cl^{2+}$	335	379	437	520sh[b]		553
M-$Co(pn)(dpt)Cl^{2+}$	339	380	437	493sh		557
y-$Co(ibn)(dpt)Cl^{2+}$	341	378	438	485sh		562
s-$Co(stien)(dpt)Cl^{2+}$		410sh	436	508		545sh
l-$Co(tmd)(dpt)Cl^{2+}$	340	372	432	514		565sh

a Wavelengths are in nanometers.

b sh = shoulder

Table 4.18

Configurational Assignments that are proposed or have been established for the $[Co(AA)(ABA)Cl]ZnCl_4 \cdot xH_2O$ Systems

(AA = en, pn, ibn, Nip-ibn, stien, tmd, Me-tmd, Bu-tmd, tmd-hex, 1,4-bn; ABA = dien, 2,3-tri, dpt)

Configuration (Fig 4.1)	I	II	IIIa	IIIb
$Co(en)(dien)Cl^{2+}$	π[78]	ω[25,26]		78
$Co(pn)(dien)Cl^{2+}$	A,D	H,I	C	B,G
$Co(ibn)(dien)Cl^{2+}$	O,Q	U,V	W	P,R
$Co(Nip\text{-}ibn)(dien)Cl^{2+}$	XI,XIII,XV			X,XII
$Co(stien)(dien)Cl^{2+}$	o,p			q,r
$Co(tmd)(dien)Cl^{2+}$	d,e,f	h	c	a,b
$Co(Me\text{-}tmd)(dien)Cl^{2+}$	IV,V		III	I,II
$Co(Bu\text{-}tmd)(dien)Cl^{2+}$	VII			VI
$Co(tmd\text{-}hex)(dien)Cl^{2+}$	VIII,IX			
$Co(1,4\text{-}bn)(dien)Cl^{2+}$	1			
$Co(2,3\text{-}tri)(en)Cl^{2+}$			Σ	η
$Co(en)(dpt)Cl^{2+}$			α[32,34]	β[32,33]
$Co(pn)(dpt)Cl^{2+}$			J,L	K,M
$Co(ibn)(dpt)Cl^{2+}$			w,z	x,y
$Co(stien)(dpt)Cl^{2+}$			s,t	u,v
$Co(tmd)(dpt)Cl^{2+}$			i,j,m,n	k,l

General Observations in $Co(AA)(dpt)X^{n+}$ Complexes

(a) Synthetic Routes: All synthetic routes product complexes of structures IIIa and IIIb only. This can be explained by (i) complexes of structures I and II being too soluble to be deposited as tetrachlorozincate(II) salts
or (ii) a rapid *cis* to *trans* isomerisation in acid and basic solutions.

(b) Visible Absorption Spectra: From the data presented in Table 4.17 it can be seen that the position of the absorption maxima (and minima) gradually progress to longer wavelengths as
(i) the ring size of the coordinated diamine increases
(ii) the amount of C-substitution on the 1,2-diamine increases.

(c) Products of Base Hydrolysis: The products of base hydrolysis are isomers of structure IIIa only.

CHAPTER 5

X-RAY STRUCTURE ANALYSES OF THE π(RACEMIC) AND *K* ISOMERS OF CHLORO(ETHYLENEDIAMINE)(DIETHYLENETRIAMINE) COBALT(III) TETRACHLOROZINCATE(II)

Introduction

In Chapters 2 and 3, the preparation and characterisation of the π, *K*, ω and "ε" isomers of the $Co(en)(dien)Cl^{2+}$ cation have been presented. The "ε" isomer has been shown to be (Chapter 3) a constant composition mixture of the π-nitro (27%) and π-chloro (73%) isomeric complexes. From a single crystal X-ray analysis[25,26], the ω isomer has been shown to have the geometric configuration II, Fig. 4.1 .

Hence the π and *K* isomers each must correspond to one of the configurations I, IIIa or IIIb, Fig. 4.1 . The π and *K* isomers have been assigned, on the basis of isomerisation reactions, the structures I and IIIb respectively (Chapter 4) and in order to confirm these assignments, the X-ray crystal structures of these isomers, as the tetrachlorozincate(II) salts, have been determined. The results indicate that the above assignments are correct.[78]

EXPERIMENTAL SECTION

(Racemic)π-Chloro(ethylenediamine)(diethylenetriamine) cobalt(III) Tetrachlorozincate(II): Racemic π-[Co(en)(dien)Cl]$ZnCl_4$ (prepared as described previously[72]) forms purple-red crystals which are stable to both air and X-rays. Precession photography, using Mo Kα and Cu Kα radiation on several samples revealed that the salt crystallises in the monoclinic system. Unit cell dimensions were obtained at 23°C by the least-squares procedure described below. A density of 1.85 (± 0.1) $g.cm^{-3}$ was obtained by flotation in methyl iodide - carbon tetrachloride solution.

Crystal Data[93] $ZnCoCl_5N_5C_6H_{21}$, formula weight 464.9; monoclinic with a = 13.745(3), b = 8.202(2), c = 15.117(6)Å, β = 98.56(1)°; V = 1686.0(Å)^3; D_{obs} = 1.85(±0.01) $g.cm^{-3}$; Z = 4; D_{calc} = 1.85 $g.cm^{-3}$; μ(mo Kα) = 32.8 cm^{-1}. The space group is $P2_1/c$ (No. 14) and was used in the alternate setting $P2_1/n$ for which conditions limiting possible reflections are: h 0 l, $h + l = 2n$; 0 k 0, $k = 2n$. In this setting the general equivalent positions are xyz; $\overline{xyz}$; 1/2 - x, 1/2 + y, 1/2 - z; 1/2 + x, 1/2 - y, 1/2 + z.

X-Ray Data Collection and Reduction: Diffraction data were collected from a well-formed crystal of centrosymmetric habit and of average diameter 0.15 mm; the ten boundary faces were $(\bar{1}\ 0\ 2)$, $(1\ 0\ \bar{2})$, $(0\ 0\ \bar{1})$, $(0\ 0\ 1)$, $(1\ 0\ \bar{1})$, $(\bar{1}\ 0\ 1)$,

($\bar{1}$ 0 0), (1 0 0), (0 $\bar{1}$ 0) and (0 1 0) and their distances from an arbitrary origin within the crystal were measured to facilitate later corrections for absorption.

The crystal was mounted in a random orientation on a Hilger and Watts computer controlled four-circle diffractometer. Twelve reflections from this crystal were accurately centred in a 3.5 mm diameter circular receiving aperture. The setting angles of these reflections were data used for a least-squares refinement[94] of cell parameters and crystal orientation, in which the wavelength of the Mo K$\bar{\alpha}$ radiation was taken as 0.71070Å.

The mosaicity of the crystal was examined by means of open-counter ω- scans at a take-off angle of 3°. The width at half-height for a typical strong, low-angle reflection was 0.14°.

The intensity data were collected with Zr filtered Mo Kα radiation at the same take-off angle. The circular receiving aperture, positioned 23 cm from the crystal, was of diameter 5 mm. Data were collected by the θ - 2θ scan technique. A symmetric scan range of 1.20° in 2θ, centred on the calculated peak position for Mo K$\bar{\alpha}$ radiation, was composed of 60 steps of 1 second duration. Stationary-crystal, stationary-counter background counts of 15 sec. were measured at each end of the scan range. Attentuation was required when the intensity of the diffracted beam exceeded 6000 counts per

second for several reflections.

An absorption correction was applied[95] using Gaussian Integration (4^3 grid points) and the transmission factors ranged from 0.62 to 0.75.

Solution and Refinement of Crystal Structure: Initial positions for the zinc and cobalt atoms were obtained from a three-dimensional Patterson synthesis. Full matrix least-squares refinement was begun using those data for which $F^2 \geqslant \sigma(F^2)$. Refinement was based on F and the function $w(|F_o| - |F_c|)^2$ was minimised. The weights, w, were taken as $4F_o^2/\sigma^2(F_o^2)$; $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The atomic scattering factors for hydrogen were taken from Stewart, Davidson and Simpson[96] and those for all other atoms and ions from the usual tabulation[97]. The effects of anomalous dispersion were included in F_c[98]; values of $\Delta f'$ and $\Delta f''$ for Zn^{2+}, Co^{3+} and Cl^- were taken from the International Tables[97].

The initial least-squares refinement, in which all atoms were assigned variable isotropic vibrational parameters, gave agreement factors $R_1 = 0.473$ and $R_2 = 0.543$, where $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and R_2 (the weighted R-factor) $= [w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$. Subsequent difference Fourier syntheses and least-squares refinements revealed the positions of all Cl, N and C atoms of the cation as well as the Cl atoms of the anion. In the final least-squares

refinement, the Zn, Co and Cl atoms were included with anisotropic vibrational parameters while the remaining eleven atoms were included with anisotropic vibrational parameters while the remaining eleven atoms were included with isotropic vibrational parameters. This refinement, using 2098 data which had $F^2 \geqslant \sigma(F^2)$, converged to give agreement factors $R_1 = 0.063$ and $R_2 = 0.068$.

A further difference Fourier synthesis showed peaks of height up to 1.2e Å^{-3} close to calculated hydrogen atom positions. In the next cycles of refinement, the twenty-one hydrogen atoms of the cation were included in their calculated positions (d(N-H) = 0.995Å, d(C-H) = 1.073Å;[97] B = 6.0Å^2); no parameters were varied for these atoms. This calculation converged with $R_1 = 0.062$ and $R_2 = 0.067$. Following recalculation of the hydrogen atom positions and the application of an absorption correction, two cycles of least-squares refinement, in which a single scale factor and 107 positional and vibrational parameters were varied, produced final agreement factors of $R_1 = 0.061$ and $R_2 = 0.066$.

Apart from twelve low angle reflections average values of the minimised function obtained after the last cycle of refinement show little dependence on $|F_o|$ or on $\lambda^{-1} \sin \theta$ which indicated that the weighting scheme is reasonable. The error in an observation of unit weight is 1.08 electrons. A final difference Fourier synthesis still shows peaks of

height up to 0.8e $\mathring{A}^{-3}$ around the Co and Zn atoms although the electron density does not rise above 0.6e $\mathring{A}^{-3}$ elsewhere or one-tenth the height of the last carbon atom located by this technique. Structure factor calculations for the 674 reflections having $F_o^2 < \sigma(F_o^2)$ show that none have $|F_o^2 - F_c^2| > \sigma(F_o)^2$. The positional and vibrational parameters and their e.s.d's obtained from the final cycle of least-squares refinement are listed in Table 5.1. In Table 5.2 are presented the root-mean-square amplitudes of vibration of the zinc, cobalt and chlorine atoms. Table 5.3 contains final values of $|F_c|$ and $|F_o|$ for the 2098 reflections which were used in the refinement. No corrections were made for secondary extinction.

K-Chloro(ethylenediamine)(diethylenetriamine)Cobalt(III) Tetrachlorozincate(II): Orange-red crystals of *K*-$[Co(en)(dien)Cl]ZnCl_4$ (prepared as described previously[72]) are stable to both air and X-rays. Precession photography, using Cu Kα and Mo Kα radiation on several samples revealed that the salt crystallises in the monoclinic system. Unit cell dimensions were obtained at 23°C by a least-squares procedure[94]. A density of 1.83 $g.cm^{-3}$ was obtained by flotation in methyl iodide - carbon tetrachloride solution.

Crystal Data: $ZnCoCl_5N_5C_6H_{21}$, formula weight 464.9; monoclinic with a = 9.676(1), b = 12.790(2), c = 13.888(3)$\mathring{A}$,

Table 5.1

Positional and Thermal Parameters for (Racemic) π-[Co(en)(dien)Cl]$ZnCl_4$

Atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zn	.25780(7)	.1714(1)	-.04905(7)	.00375(6)	.0125(2)	.00266(5)	-.00083(9)	.00095(4)	.00014(8)
Co	.02122(8)	.2407(1)	.22607(7)	.00271(6)	.0087(2)	.00243(5)	.0001(1)	.00091(4)	.00000(9)
Cl_1	.0981(2)	.2279(3)	-.1035(2)	.0040(1)	.0135(5)	.0043(1)	-.0009(2)	-.0001(1)	.0003(2)
Cl_2	.2532(2)	.0731(3)	.0892(2)	.0059(2)	.0175(5)	.0032(1)	.0034(2)	.0019(1)	.0022(2)
Cl_3	.3565(2)	.3894(3)	-.0474(2)	.0049(2)	.0150(5)	.0043(1)	-.0031(2)	.0019(1)	-.0018(2)
Cl_4	.3139(2)	-.0145(4)	-.1414(2)	.0073(2)	.0150(5)	.0047(1)	-.0020(3)	.0034(1)	-.0021(2)
Cl_5	.1199(2)	.4361(3)	.1845(2)	.0038(1)	.0121(4)	.0039(1)	-.0019(2)	.0010(1)	.0005(2)

Atom	x	y	z	B(Å^2)	Atom	x	y	z	B(Å^2)
N_1	.0072(5)	.1551(9)	.1038(4)	2.5(1)	C_2	.3601(8)	.174(1)	.5944(7)	4.5(2)
N_2	.4059(5)	.1231(9)	.6823(5)	2.9(1)	C_3	.1072(7)	.230(1)	.4127(6)	3.1(2)
N_3	.5374(5)	.1623(9)	.8447(4)	2.6(1)	C_4	.1821(6)	.163(1)	.3592(6)	2.7(2)
N_4	.1363(5)	.1031(9)	.2695(4)	2.5(1)	C_5	.8976(7)	.076(1)	.7308(6)	3.4(2)
N_5	.9377(5)	.0627(9)	.2639(5)	2.8(1)	C_6	.0002(6)	.080(1)	.6927(6)	2.9(2)
C_1	.4322(8)	.238(1)	.5421(7)	4.6(2)					

[a] The expression used for the atomic temperature factor was $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$

Table 5.2

Root-Mean-Square Amplitudes of Vibration (Å) for

π-[Co(en)(dien)Cl]$ZnCl_4$

Atom	Minimum	Intermediate	Maximum
ZN	.160(2)	.190(2)	.212(2)
Co	.141(2)	.172(2)	.177(2)
Cl_1	.182(4)	.211(4)	.236(3)
Cl_2	.163(4)	.195(4)	.286(4)
Cl_3	.172(4)	.198(4)	.272(3)
Cl_4	.169(4)	.213(4)	.302(4)
Cl_5	.156(4)	.214(3)	.223(4)

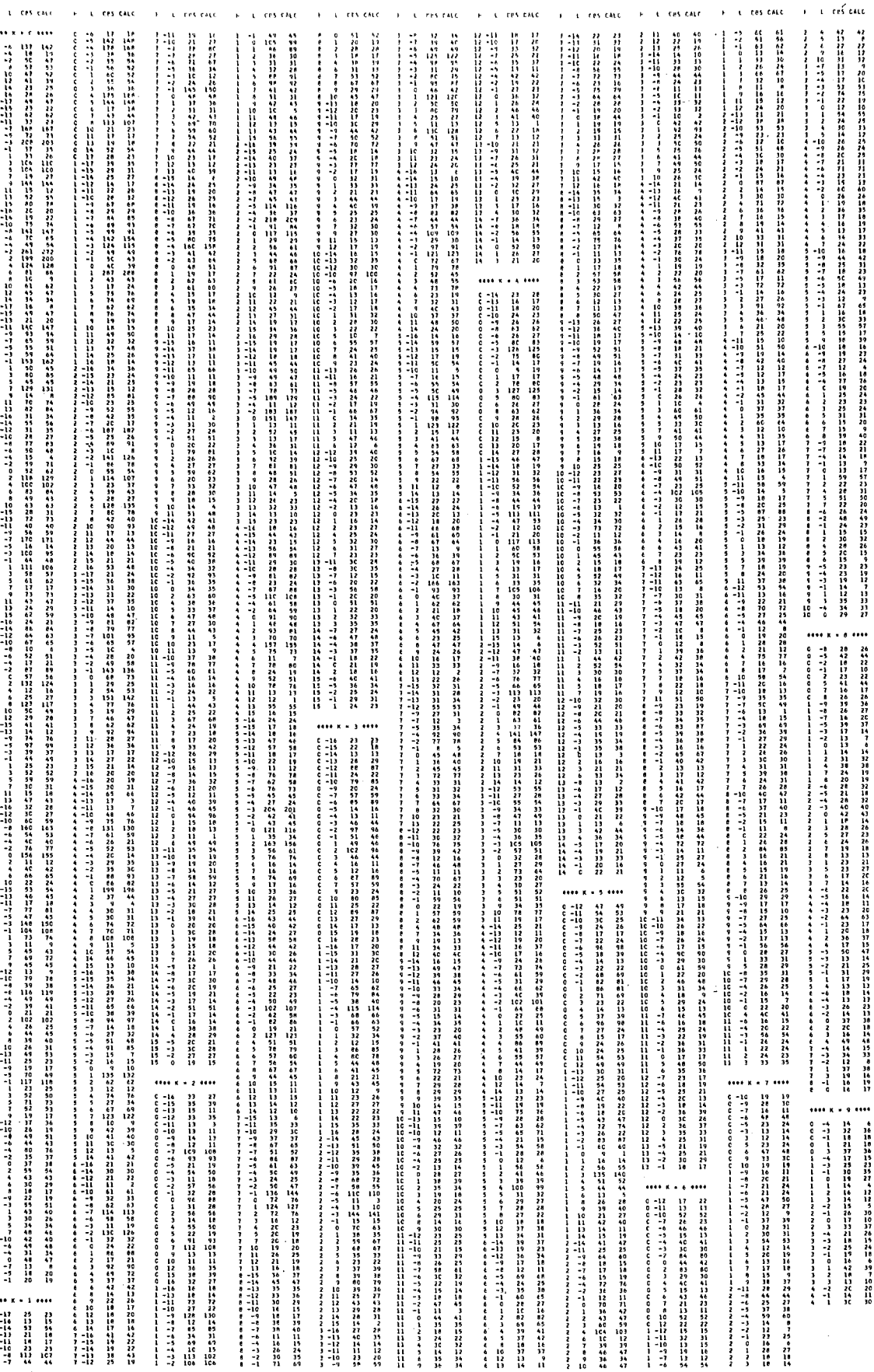


Table 5.3 Observed and Calculated Structure Amplitudes for π- [Co(en)(dien)Cl]$ZnCl_4$.

$\beta = 93.63(1)^{\circ}$, $\underline{V} = 1715.2(\mathring{A})^3$; $\underline{D}_{obs} = 1.83(\ 0.01)\ g.cm^{-3}$; $\underline{Z} = 4$; $\underline{D}_{calc} = 1.83\ g.cm^{-1}$; μ(mo Kα) = 32.8 cm^{-1}. Two space groups (Cc acentric and C2/c centrosymmetric) were consistent with the observed conditions limiting possible reflections ($\underline{h}\ \underline{k}\ \underline{l}$, $\underline{h}+\underline{k} = 2\underline{n}$; $\underline{h}\ 0\ \underline{l}$, $\underline{l} = 2\underline{n}$). Exact crystallographic symmetry could not be imposed on conceivable cationic structures so that the acentric possibility was considered correct.

X-Ray Data Collection and Reduction: Diffraction data were collected from a well-formed crystal of non-centrosymmetric habit and average diameter 0.3 mm; the ten boundary faces were $(\bar{1}\ \bar{1}\ \bar{1})$, $(\bar{1}\ 1\ \bar{1})$, $(\bar{1}\ 1\ 1)$, $(\bar{1}\ \bar{1}\ 1)$, $(1\ 1\ 1)$, $(1\ 1\ 0)$, $(1\ 1\ \bar{1})$, $(1\ \bar{1}\ \bar{1})$, $(1\ \bar{1}\ 0)$ and $(1\ \bar{1}\ 1)$ and the necessary measurements were made to enable accurate absorption corrections to be applied.

The crystal was mounted, and a data set collected using the same techniques as those described for the π isomer, except that the mosaicity for a typical strong, low angle reflection was 0.09°.

The intensities of 1708 unique reflections, with $2\theta \leqslant 50^{\circ}$, were recorded and processed. The 1507 intensities $\geqslant 3\sigma$ were then collected again in the strictly equivalent form using a symmetric scan range of 1.60° in 2θ with 80 one-second steps.

The intensities of three reflections which were monitored at regular intervals showed only the deviations from the mean predicted by counting statistics.

Solution and Refinement of the Crystal Structure: The structure has been successfully solved and refined in space group Cc. Positions for the zinc and cobalt atoms were obtained from a three-dimensional Patterson synthesis. The origin of the unit cell was originally fixed by choosing the position of the cobalt atom to be (0, y, 0) and varying the y parameter only for this atom. Initial least-squares refinement, in which these atoms were assigned variable isotropic vibrational parameters, gave agreement factors $R_1 = 0.375$ and $R_2 = 0.443$.

Two subsequent difference Fourier syntheses revealed the positions of all Cl, N and C atoms for the cation, as well as the Cl atoms of the anion. This map did not show regions of high electron density around the Zn and Co atoms and isotropic temperature factors were used for all atoms throughout the analysis. This refinement converged to give agreement factors $R_1 = 0.067$ and $R_2 = 0.084$. For convenience, the coordinates of all of the atoms were transformed so that those of the Zn atom were (0, y, 0). In all subsequent least-squares refinements, the effects of anomalous dispersion were included in F_c[97,98]. These calculations were used to determine the polarity of the space group,

using the coordinates obtained above, and coordinates obtained by inverting the structure through the origin. The same scale factor and isotropic vibrational parameters were used in each calculation. The resulting agreement factors were R_1 = 0.072 and R_2 = 0.091 for one structure, and R_1 = 0.069 and R_2 = 0.088 for the other. The coordinates xyz (Table 5.4) define the polarity of the space group and were used in the final refinements.

In the next cycles of refinement, the twenty-one hydrogen atoms of the cation were included in their calculated positions (d(N-H) = 0.995Å, d(C-H) = 1.073Å, H-X-H = 109.5°;[97] B = 8.0Å^2); no parameters were varied for these atoms. This calculation converged with R_1 = 0.062 and R_2 = 0.078. An absorption correction was applied using Gaussian integration (4^3 grid points) with transmission factors ranging from 0.44 to 0.57 and, after averaging the equivalent forms, the data set consisted of 1592 reflections of which 1355 had intensities of $\geq 3\sigma$.

Following recalculation of the hydrogen positions, two cycles of least-squares refinement, in which a single scale

Table 5.4

Positional and Thermal Parameters for K-[Co(en)(dien)Cl]$ZnCl_4$

Atom	x	y	z	B(Å^2)
Zn	1.00000	1.0149(1)	1.00000	2.55(3)
Co	1.4400(3)	0.8323(1)	1.2700(2)	1.69(3)
Cl_1	1.1684(5)	1.1156(3)	1.0764(3)	2.73(6)
Cl_2	1.0373(5)	1.0083(3)	0.8402(3)	3.67(8)
Cl_3	0.7949(5)	1.0919(3)	1.0229(3)	3.35(7)
Cl_4	1.0074(5)	0.8482(3)	1.0580(3)	3.22(7)
Cl_5	1.4844(5)	0.9966(3)	1.3251(3)	3.14(7)
N_1	1.379(1)	0.6915(9)	1.2306(8)	2.2(2)
N_2	1.296(1)	0.824(1)	1.3636(9)	2.5(2)
N_3	1.589(1)	0.781(1)	1.3630(1)	2.9(2)
N_4	1.581(1)	0.8346(9)	1.1774(9)	2.4(2)
N_5	1.320(1)	0.894(1)	1.1651(9)	2.7(2)
C_1	1.239(2)	0.675(1)	1.265(1)	4.0(3)
C_2	1.231(2)	0.718(1)	1.361(1)	4.1(3)
C_3	1.716(2)	0.761(1)	1.311(1)	3.4(3)
C_4	1.721(2)	0.839(1)	1.228(1)	3.6(3)
C_5	1.546(2)	0.911(1)	1.103(1)	4.0(3)
C_6	1.393(2)	0.895(1)	1.075(1)	3.8(3)

factor and 70 positional and vibrational parameters were varied, produced final agreement factors of $R_1 = 0.057$ and $R_2 = 0.071$.

Average values of the minimised function obtained after the final cycle of refinement show very little dependence on $|F_o|$ or on $\lambda^{-1} \sin\theta$, which indicates that the relative weighting scheme is reasonable. A final difference Fourier synthesis still contains peaks of height up to 3.95 e Å^{-3} around the Zn, Co and Cl atoms although the electron density does not rise above 1.0 e Å^{-3}, or 0.15 of the last carbon atom located by this technique. Structure factor calculations for the 239 reflections having $F_o^2 < 3\sigma(F_o^2)$ show that none have $|F_o^2 - F_c^2| > 3\sigma(F_o)^2$.

The positional and vibrational parameters and their e.s.d.'s obtained from the final cycle of least-squares refinement are listed in Table 5.4. Table 5.5 contains the final values of $|F_o|$ and $|F_c|$ for the 1353 reflections which were used in the refinement. There is no evidence for secondary extinction and no corrections were made.

Anisotropic thermal parameters were not refined since such expensive calculations were not expected to reveal any further points of chemical interest.[99]

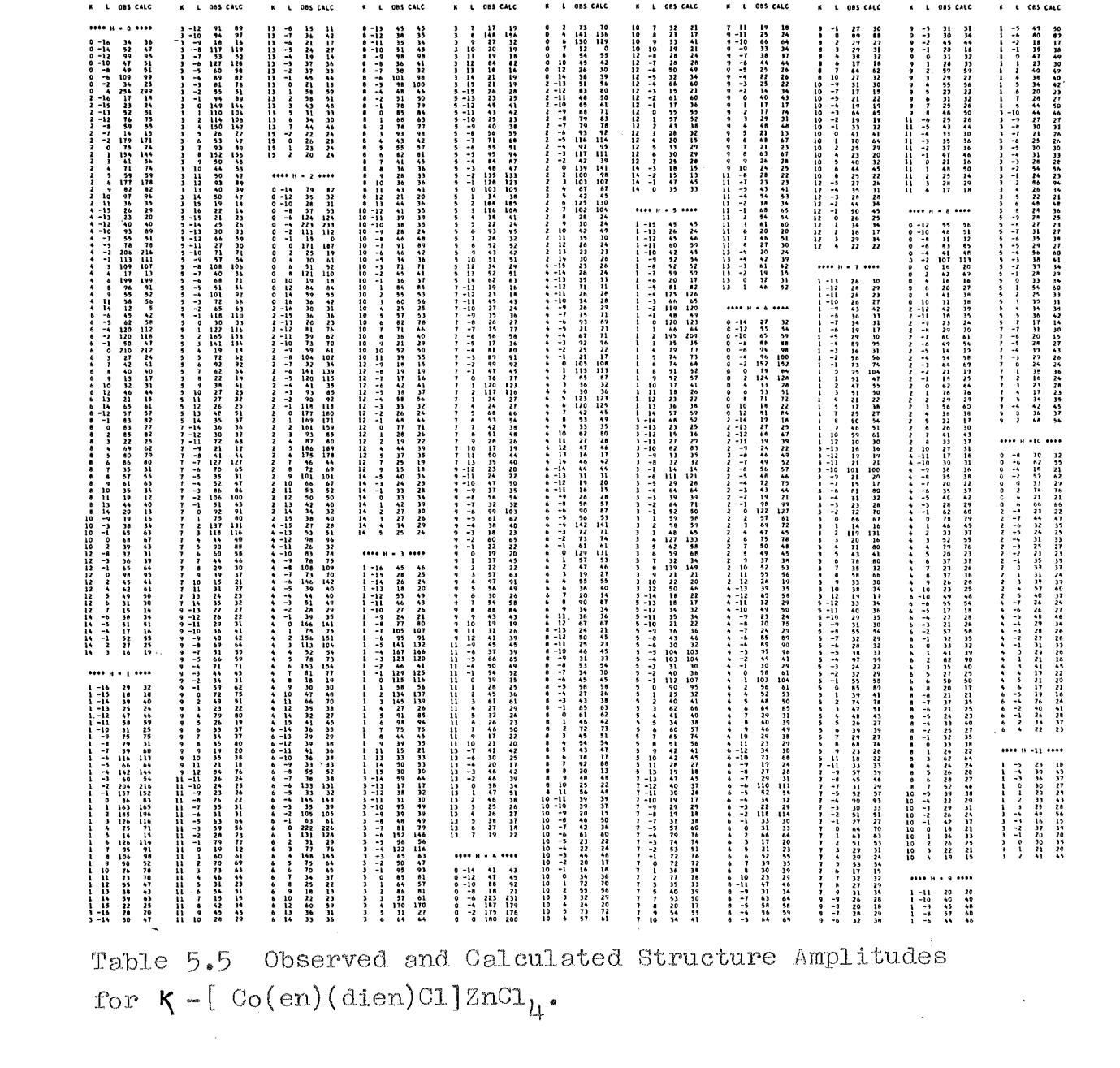


Table 5.5 Observed and Calculated Structure Amplitudes for K-[Co(en)(dien)Cl]$ZnCl_4$.

DESCRIPTION OF THE CRYSTAL STRUCTURES

The structure analysis has revealed that, for the π isomer, the crystals contain an equimolar mixture of two enantiomorphic cations, together with tetrachlorozincate(II) anions, linked by electrostatic and Van der Waals forces. Similar results have been obtained for the *K* isomer, except that the cation is optically inactive. Perspective views of the complex cations are presented in Figures 5.1-5.3, while the $ZnCl_4^{2-}$ anion, as it occurs in the π isomer, is shown in Figure 5.4. Figure 5.5 shows the arrangement of ions with respect to the unit cell for the π isomer and Figure 5.6 is a similar diagram for the *K* isomer.

Description of the $Co(en)(dien)Cl^{2+}$ Cations: Figures 5.1, 5.2 and 5.3 present perspective views of the π and *K*-$Co(en)(dienCl^{2+}$ cations and indicate the atom numbering systems. As expected, for both cations, the dien ligand is coordinated tridentate, the en ligand bidentate and the coordinated chloride completes the coordination sphere. For the π isomer, the geometry of the complex is of type I (Fig. 4.1), with the nitrogen atoms of the dien ligand in a facial configuration. For the *K* isomer, the geometry is of type IIIb with the hydrogen atom bonded to the secondary amine of the peripher al dien ligand being remote from the chloride ligand (a similar arrangement occurs in the

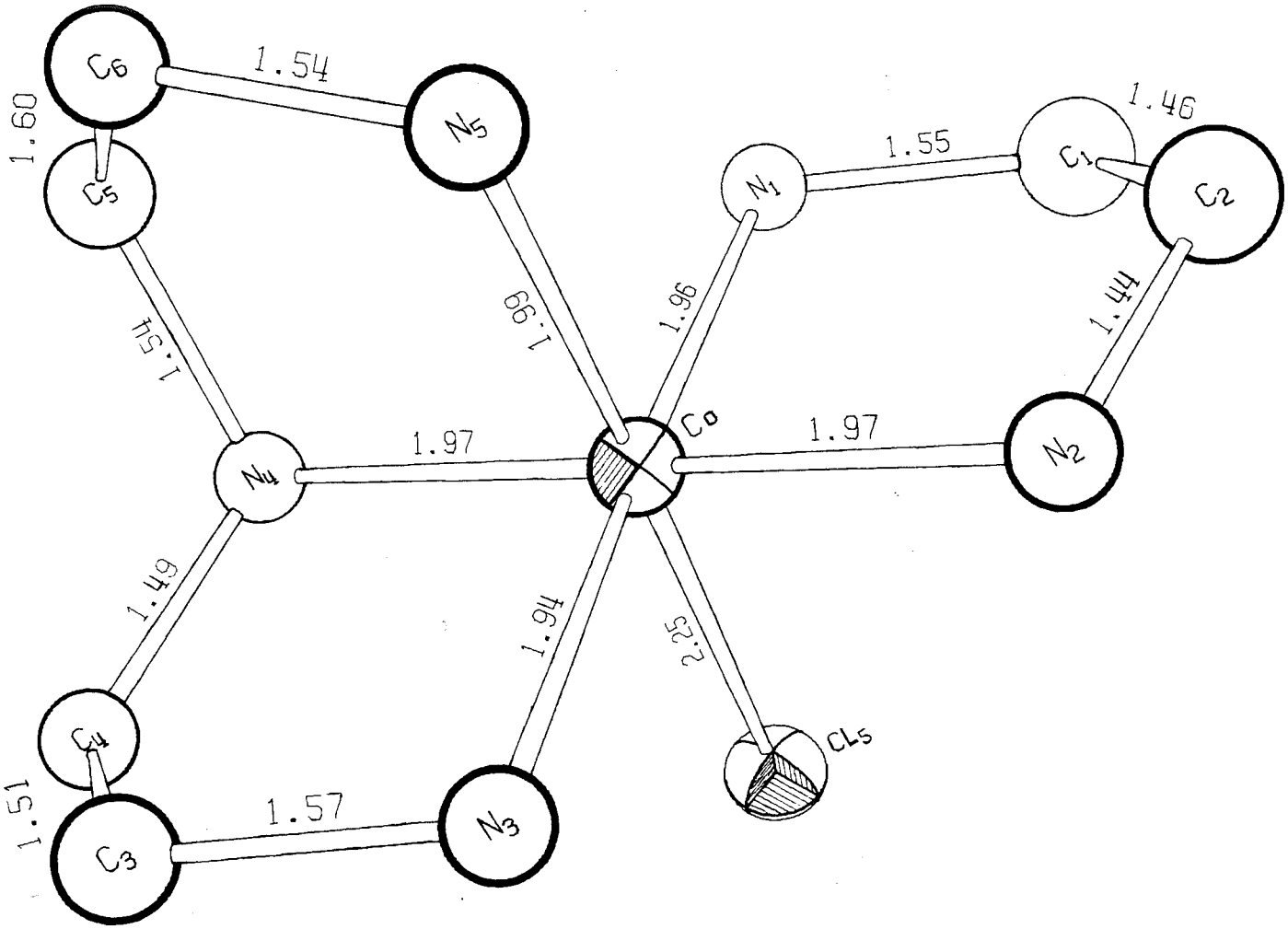


Figure 5.1 A perspective view of the π- Co(en)(dien)Cl^{2+} cation showing the atom numbering scheme. Bond lengths are in Å.

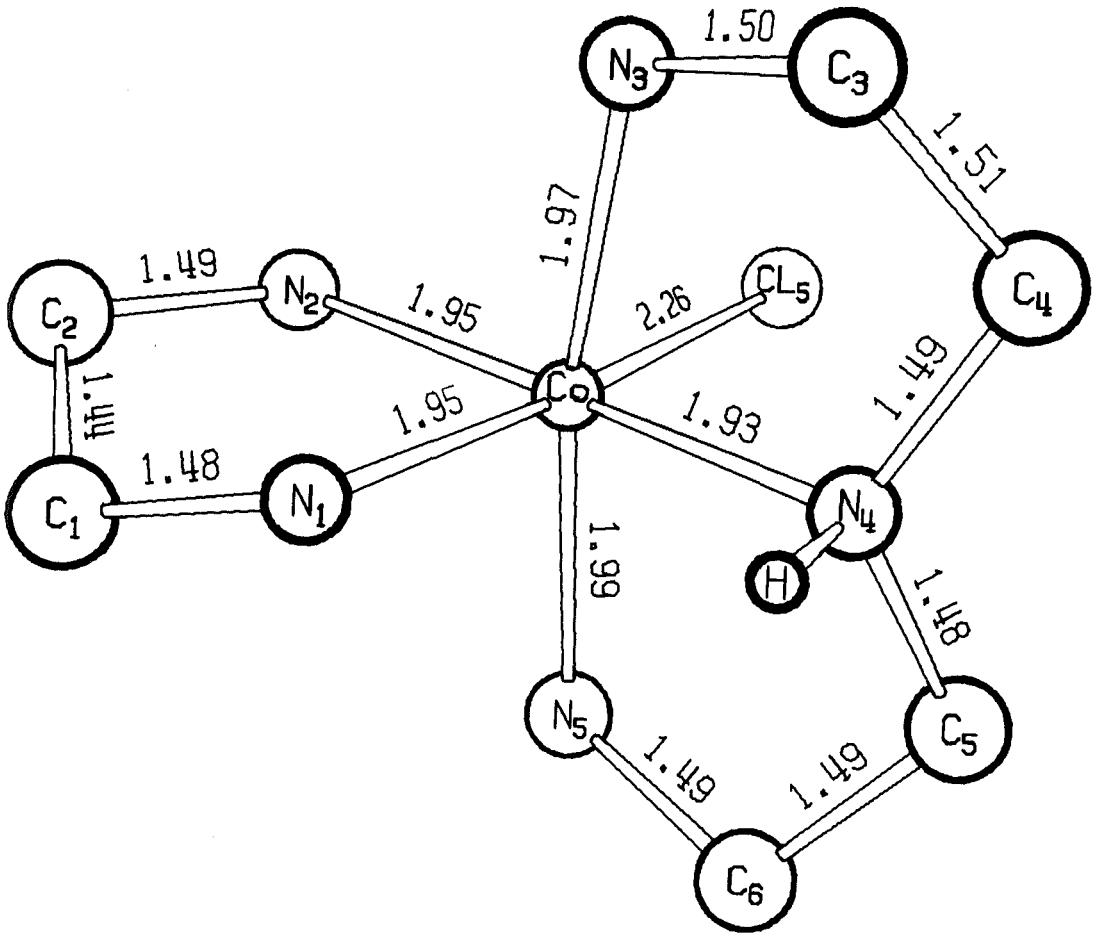


Figure 5.2 A general view of the κ - $Co(en)(dien)Cl^{2+}$ cation showing the atom numbering scheme. Bond lengths are in Å.

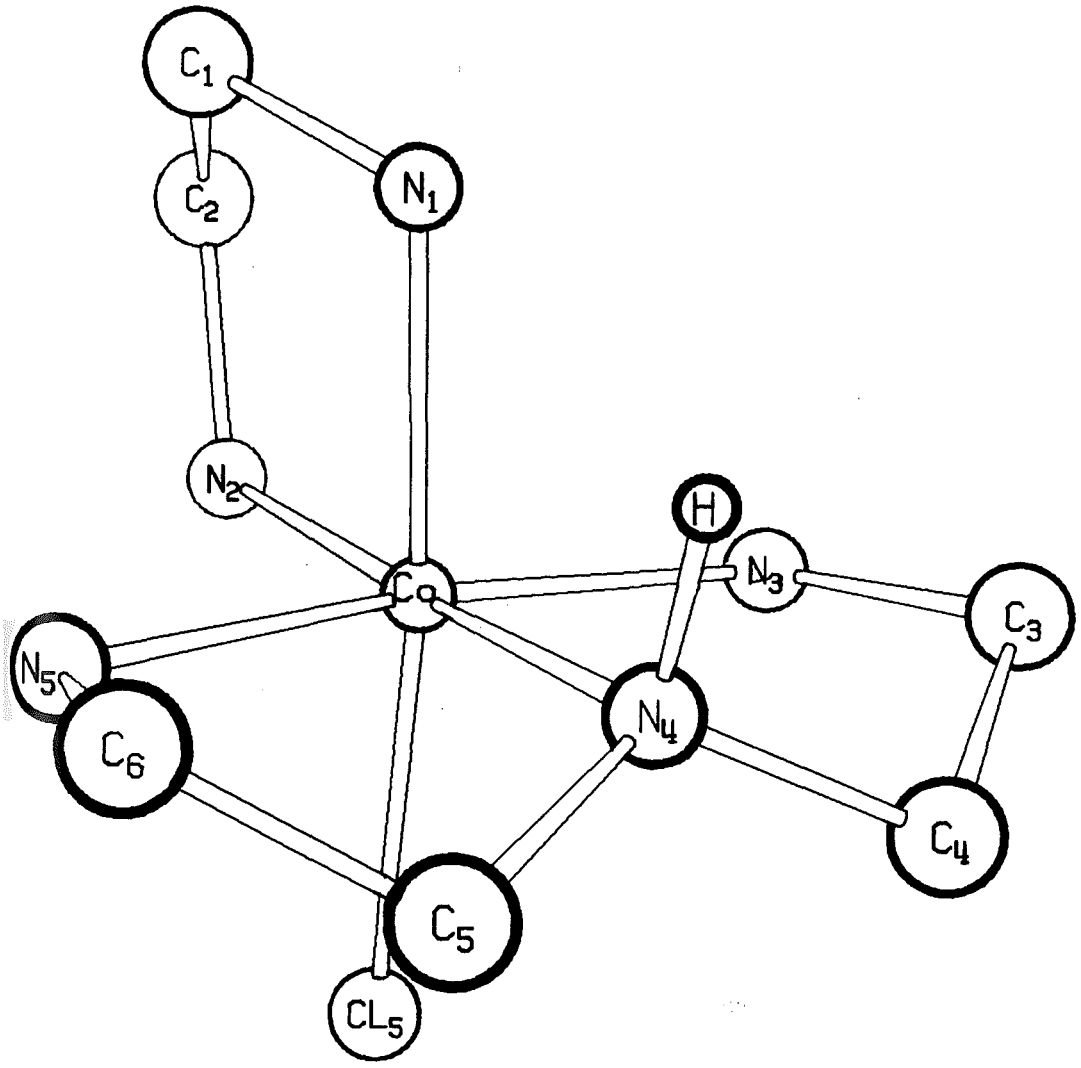


Figure 5.3 A perspective view of the κ - $Co(en)(dien)Cl^{2+}$ cation.

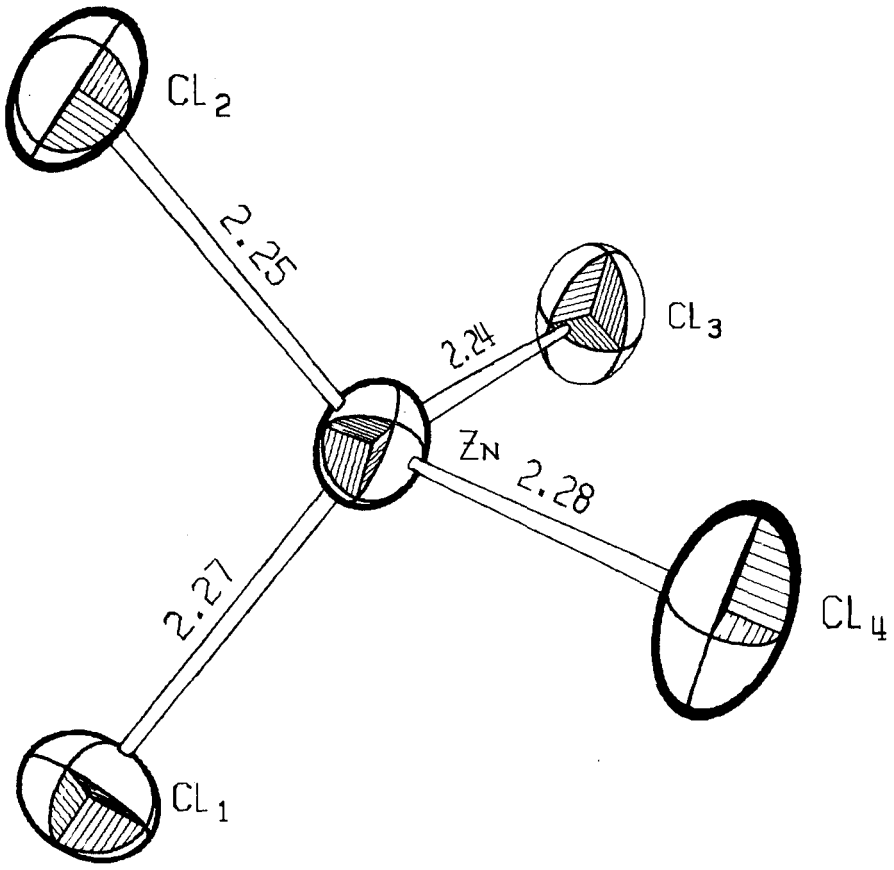


Figure 5.4 A perspective view of the $ZnCl_4^{2-}$ anion in π-[Co(en)(dien)Cl]$ZnCl_4$ showing the atom numbering scheme. A similar numbering system is used for the $ZnCl_4^{2-}$ anion in the κ isomer. Bond lengths are in Å.

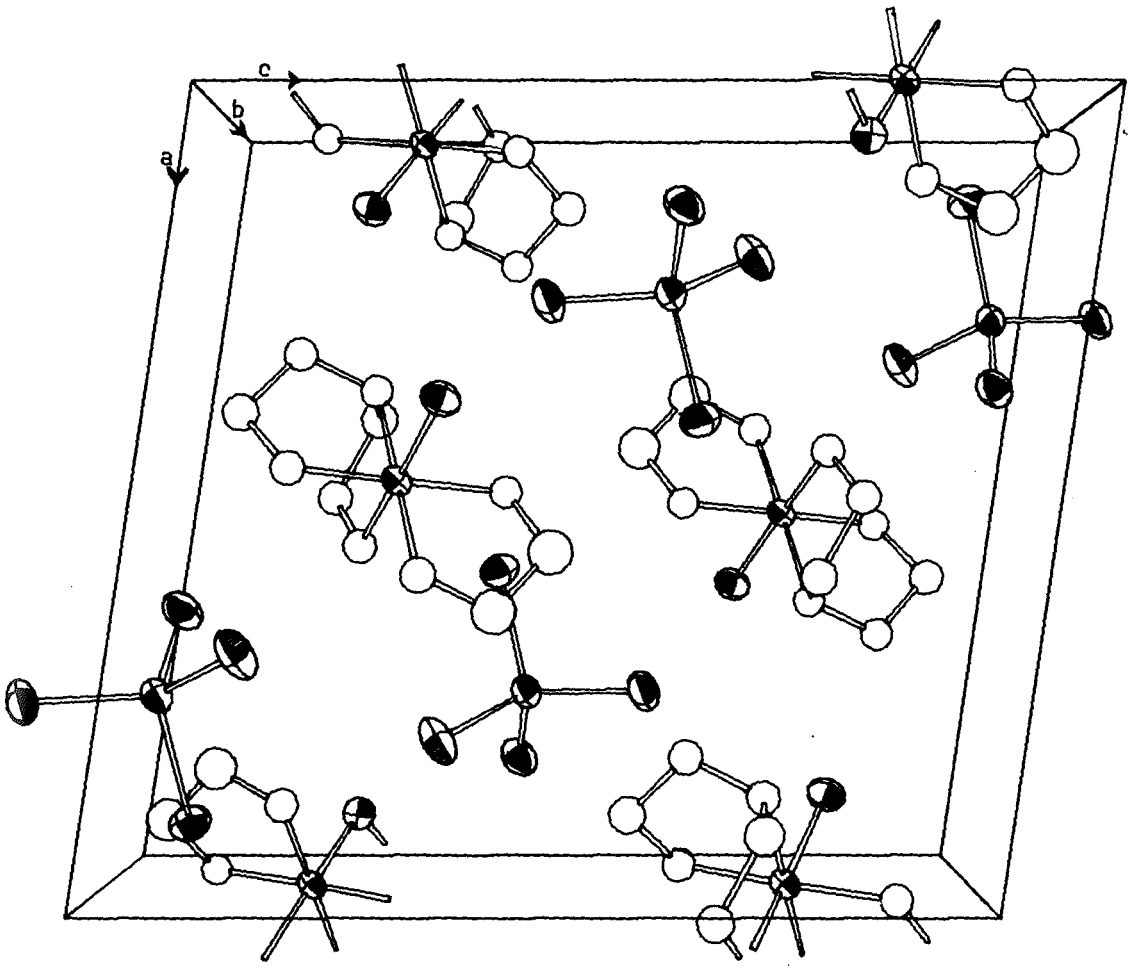


Figure 5.5 The packing of the ions in π- $[Co(en)(dien)Cl]ZnCl_4$ as viewed down the b axis.

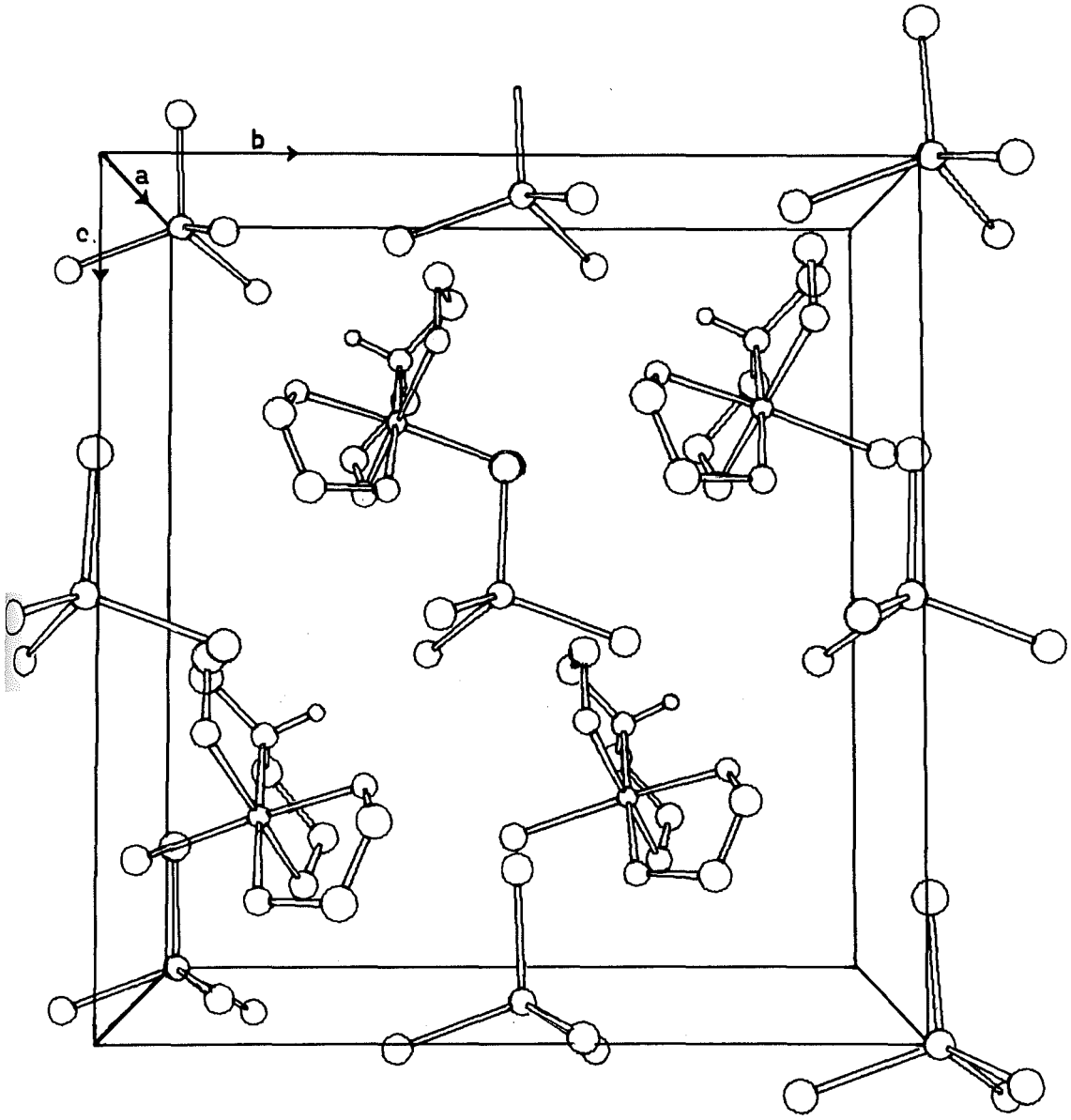


Figure 5.6 The packing of the ions in κ-[Co(en)(dien)Cl]$ZnCl_4$ as viewed down the a axis.

β-Co(en)(dpt)Cl^{2+} cation[33]).

Intramolecular bond distances and angles within the complex cations are presented in Tables 5.6 (π isomer) and 5.7 (*K* isomer). The mean Co(III)-N bond distance for the π isomer is 1.97(4)Å, and comparable distances for related complexes are 1.955(5)Å in racemic α-[Co(trien)(NH_3)Cl](NO_3)$_2$,[22] 1.955Å in Λ-β_2-(SSS)-[Co(trien)(S-pro)]$ZnCl_4$,[100] 1.967(6)Å in αα-[Co(tetren)Cl]Cl.ClO_4,[16] 1.99(2)Å in β-[Co(en)(dpt)Cl]$ZnCl_4$,[33] and 1.95(5)Å in α-[Co(en)(dpt)Cl]I_2.H_2O.[34]

For the *K* isomer, the mean Co(III)-N(primary) bond distance is 1.97(2)Å and this is comparable with the values in the complexes quoted above. However, the Co(III)-N(secondary) bond distance (1.93(1)Å) is significantly shorter than the mean Co(III)-N(primary) bond length. Also the N(3)-Co-N(5) bond angle is 169.6(5)°, a significant deviation from 180°. Even greater Cu-N(secondary) bond length deviations and N-Cu-N angular distortions are found for some peripheral Cu(II) dien complexes.[101-103]

An increase in the N(3)-Co-N(5) angle to 180° would result in a decrease in the Co-N(secondary) bond distance and the observed values are probably a balance between these two effects. These distortions are not found in the peripherial Co(en)(dpt)Cl^{2+} isomers[33,34], presumably because the strain is relieved by the larger size of the six-membered chelate rings.

Table 5.6

Intramolecular Bond Distances and Angles for the

π-Co(en)(dien)Cl^{2+} Cation

Intramolecular Bond Distances

Atoms	Distance, Å	Atoms	Distance, Å
Co - Cl_5	2.249(3)	C_2 - N_2	1.44(1)
Co - N_1	1.960(7)	N_3 - C_3	1.57(1)
Co - N_2	1.971(7)	C_3 - C_4	1.51(1)
Co - N_3	1.944(7)	C_4 - N_4	1.49(1)
Co - N_4	1.974(7)	N_4 - C_5	1.54(1)
Co - N_5	1.993(7)	C_5 - C_6	1.60(1)
N_1 - C_1	1.55(1)	C_6 - N_5	1.54(1)
C_1 - C_2	1.46(1)		

Intramolecular Bond Angles

Atoms	Angle, deg.	Atoms	Angle, deg.
Cl_5 - Co - N_1	88.3(2)	Co - N_1 - C_1	109.1(6)
Cl_5 - Co - N_2	89.5(2)	N_1 - C_1 - C_2	108.9(8)
Cl_5 - Co - N_3	88.6(2)	C_1 - C_2 - N_2	111.4(9)
Cl_5 - Co - N_4	90.8(2)	C_2 - N_2 - Co	111.4(6)
Cl_5 - Co - N_5	178.1(2)	CO - N_3 - C_3	110.4(5)
N_1 - Co - N_2	85.7(3)	N_3 - C_3 - C_4	104.8(7)
N_1 - Co - N_3	176.7(3)	C_3 - C_4 - N_4	112.2(7)
N_1 - Co - N_4	94.0(3)	C_4 - N_4 - Co	109.0(5)
N_1 - Co - N_5	91.6(3)	Co - N_4 - C_5	108.6(5)
N_2 - Co - N_3	93.1(3)	C_4 - N_4 - C_5	113.6(7)
N_2 - Co - N_4	179.6(3)	N_4 - C_5 - C_6	107.3(7)
N_2 - Co - N_5	92.4(3)	C_5 - C_6 - N_5	107.2(7)
N_3 - Co - N_4	87.2(3)	C_6 - N_5 - Co	111.9(5)
N_3 - Co - N_5	91.5(3)		
N_4 - Co - N_5	87.3(3)		

Table 5.7

Intramolecular Bond Distances and Angles for the

K-Co(en)(dien)Cl^{2+} Cation

Intramolecular Bond Distances

Atoms	Distance, Å	Atoms	Distance, Å
Co - Cl_5	2.268(4)	C_2 - N_2	1.49(2)
Co - N_1	1.96(1)	N_3 - C_3	1.49(2)
Co - N_2	1.95(1)	C_3 - C_4	1.53(2)
Co - N_3	1.98(1)	C_4 - N_4	1.49(2)
Co - N_4	1.93(1)	N_4 - C_5	1.45(2)
Co - N_5	1.97(1)	C_5 - C_6	1.51(3)
N_1 - C_1	1.48(2)	C_6 - N_5	1.47(2)
C_1 - C_2	1.44(3)		

Intramolecular Bond Angles

Atoms	Angle, deg.	Atoms	Angle, deg.
Cl_5 - Co - N_1	172.5(4)	Co - N_1 - C_1	108.1(9)
Cl_5 - Co - N_2	87.7(4)	N_1 - C_1 - C_2	109(1)
Cl_5 - Co - N_3	88.4(4)	C_1 - C_2 - N_2	108(1)
Cl_5 - Co - N_4	94.8(4)	C_2 - N_2 - Co	111(1)
Cl_5 - Co - N_5	88.2(4)	Co - N_3 - C_3	109.6(9)
N_1 - Co - N_2	85.1(5)	N_3 - C_3 - C_4	108(1)
N_1 - Co - N_3	94.1(5)	C_3 - C_4 - N_4	105(1)
N_1 - Co - N_4	92.4(5)	C_4 - N_4 - Co	110.4(9)
N_1 - Co - N_5	90.5(5)	Co - N_4 - C_5	110(1)
N_2 - Co - N_3	94.3(5)	C_4 - N_4 - C_5	118(1)
N_2 - Co - N_4	177.5(5)	N_4 - C_5 - C_6	105(1)
N_2 - Co - N_5	95.4(5)	C_5 - C_6 - N_5	107(1)
N_3 - Co - N_4	85.6(6)	C_6 - N_5 - Co	109(1)
N_3 - Co - N_5	169.6(5)		
N_4 - Co - N_5	84.9(5)		

The Co-Cl(5) bond distances are 2.249(3)Å (π isomer) and 2.268(4)Å (*K* isomer). Comparable distances for related complexes are 2.271(2)Å in α-$[Co(trien)NH_3Cl](NO_3)_2$,[22] 2.286(2)Å in $[Co(NH_3)_5Cl]Cl_2$,[104] 2.237(4)Å in β-$[Co(trien)(OH_2)Cl](ClO_4)_2$,[105] 2.259(9)Å in β-$[Co(en)(dpt)Cl]ZnCl_4$,[33] 2.263(3)Å in $\alpha\alpha$-$[Co(tetren)Cl]Cl.ClO_4$,[16] and 2.21(2)Å in α-$[Co(en)(dpt)Cl]I_2.H_2O$[34].

For the π isomer, the angles subtended at the cobalt atom by the two dien chelate rings (87.2(3) and 87.3(3)°) are equal within probable limits of error. However, the angle subtended by the en chelate ring is very significantly contracted (85.7(3)°) from the angles subtended by each of the other rings. Nevertheless, all of these angles are within the range of values found in other Co(III)-C_2 bridged polyamine complexes[22,33,34,100,105]. These chelate angles combine to produce significant distortions from regular octahedral coordination about the central cobalt atom (Table 5.6).

In the *K* isomer, the angles subtended at the cobalt atom by the two dien chelate rings (85.6(6) and 84.9(5)°) are equal but they are significantly contracted from the values obtained for the π isomer. Comparable values are 78.8(6), 82.0(4) and 81.9(4), 81.8(5)° in $[Cu(dien)_2]Br_2.H_2O$,[102] and 85.2(3), 85.0(3)° in $Cu(dien)C_2O_4.4H_2O$[103]. The above copper(II) complexes are expected to have smaller

angles because the mean Cu-N bond distances (2.237(12)Å primary nitrogen atoms, 2.010(11)Å secondary nitrogen atoms) are larger than the mean Co-N bond distances (1.97(2)Å primary nitrogen atoms, 1.93(1)Å secondary nitrogen atom).

The range of C-N and C-C bond distances is similar to that found in other Co(III)-en complexes[33,34,106]. For the π isomer, the C(5)-C(6) bond distance (1.60(1)Å) is expanded significantly from the C(3)-C(4) bond distance (1.51(1)Å) showing the effects of chelate ring distortion in the facial configuration of the dien ligand and of non-bonded interactions with the anion (see later). A similar, though less marked effect is observed in facial $Cr(dien)Cl_3$[64].

In the *K* isomer, the C(3)-C(4) and C(5)-C(6) bond distances (1.53(2) and 1.51(3)Å respectively) are not significantly different. This is expected as the dien chelate ring is coordinated in a near symmetrical orientation with respect to the en chelate ring.

Significant angular distortions occur at the secondary nitrogen atom in the dien ligand: C(4)-N(4)-C(5), 113.6(7)° (π); 118(1)° (*K*). The angle in the facial π isomer can be compared with similar angular distortions where "bends" occur in the chain of a coordinated polyamine ligand, e.g. αα-$Co(tetren)Cl^{2+}$ (113.7(9), 114.0(10), 112.5(9)°)[16] and α- $Co(trien)NH_3Cl^{2+}$ (113.1(6), 114.0(6)°)[22]. Comparative angles for the peripheral *K* isomer can be found in

$[Cu(dien)_2](NO_3)_2$ (115.3(11), 115.1(13)°)[101], $[Cu(dien)_2]Br_2.H_2O$ (117.4(26),111.3(22)°)[102], $Cu(dien)C_2O_4.4H_2O$ (112.6(8)°)[103], and β-$[Co(trien)(gly)]I_2.0.5H_2O$ (117.8(7)°, Δ-β_1-RS-isomer)[107].

As is evident from Figures 5.1 and 5.3 the chelate rings are considerably puckered, the effect being more marked in the *K* isomer. For this isomer, torsion angles[108] about the C-C bonds of the five-membered rings are C(1)-C(2) (en), -45(2)°; C(3)-C(4) (dien), 48(2)°; C(5)-C(6) (dien), -49(2)°. Observed torsion angles in other $-NH(CH_2)_2NH-$ chelate rings are 65(5)° and 60(9)° in the isomeric $Co(en)(dpt)Cl^{2+}$ cations[33,34], and 46.5, 37.2, 44.9° and 49.2, 41.6, 38.7, 50.6° in the α-trien[22] and αβS-tetren[15] chelate rings, respectively. Thus, the observed degree of ring puckering is typical for five-membered Co(III) polyamine complexes and indicates that the anion is symmetrically placed with respect to the tridentate plane so as to have little non-bonded effect (Table 5.8). Non-bonded interactions with the hydrogen atoms on the polyamine ligands appear to be of minor importance when the amine is in the peripheral configuration.

However, the torsion angles[108] about the C-C bonds of the five-membered rings in the π isomer are C(1)-C(2) (en), 14.3(8)°; C(3)-C(4) (dien), 15.3(6)°; C(5)-C(6) (dien), -2.6(1)°. These are very much smaller than those observed

Table 5.8

Close Contacts in the K-[Co(en)(dien)Cl]$ZnCl_4$ Crystal

Atoms X ... Y	d(X ... Y), Å	Atoms X ... Y	d(X ...Y), Å
Cl_1 ... N_4	3.27(1)	Cl_2 ... N_2	3.30(1)
Cl_1 ... N_2	3.39(1)	Cl_2 ... N_1	3.30(1)
Cl_1 ... N_5	3.39(1)	Cl_2 ... N_3	3.75(1)
Cl_1 ... C_4	3.56(1)	Cl_2 ... C_1	3.81(2)
Cl_1 ... C_6	3.56(1)	Cl_2 ... C_4	3.88(2)
Cl_1 ... C_3	3.75(1)	Cl_2 ... C_3	3.89(2)
Cl_1 ... C_2	3.76(1)	Cl_2 ... N_5	3.97(1)
Cl_1 ... N_1	3.76(1)	Cl_2 ... C_2	3.98(2)
Cl_1 ... C_5	3.98(2)		
Cl_3 ... N_1	3.21(1)	Cl_4 ... N_3	3.32(1)
Cl_3 ... N_3	3.32(1)	Cl_4 ... N_5	3.34(1)
Cl_3 ... C_3	3.54(2)	Cl_4 ... C_4	3.75(2)
Cl_3 ... C_5	3.57(2)	Cl_4 ... C_6	3.78(2)
Cl_3 ... C_1	3.60(2)	Cl_4 ... C_2	3.80(2)
		Cl_4 ... N_2	3.96(1)

for other systems (e.g. the corresponding dien torsion angles in facial $Cr(dien)Cl_3$[64] are 47.6 and -44.3° [109]), indicating that the degree of ring puckering is small. Table 5.9 presents the close interionic contact distances in the π-$[Co(en)(dien)Cl]ZnCl_4$ crystal. There are thirteen vectors between anion and cation atoms that are less than 3.5Å and these all involve the tetrachlorozincate(II) chlorine atoms. Their combined effect is to distort the chelate rings and to produce the small torsion angles observed. A low torsion angle is also observed in the αβR-tetren chelate ring, and is attributed to close contact of the perchlorate anion[15]. Non-bonded interactions with the hydrogen atoms on the ligands are also thought to be important, especially as the dien ligand is in the facial configuration. Indeed, models indicate that the configuration having the least non-bonded interactions (en protons with dien protons) has the Co-N(4)-C(5)-C(6)-N(5) ring nearly planar.

The Tetrachlorozincate(II) Anion: A perspective view of the tetrachlorozincate(II) anion (as it occurs in the π isomer) is presented in Figure 5.4. In both isomers, a slightly distorted tetrahedral arrangement of chlorine atoms about the central zinc atom is observed (Table 5.10), with mean Zn-Cl bond distances of 2.26(3)Å (π) and 2.27(1)Å (*K*). Comparable values in related compounds are 2.264(17)Å in

Table 5.9

Close Contacts in the π-[Co(en)(dien)Cl]$ZnCl_4$ Crystal

Atoms X ... Y	d(X ... Y), Å	Atoms X ... Y	d(X ... Y), Å
Cl_1 ... N_5	3.384(8)	Cl_3 ... N_5	3.238(7)
Cl_1 ... C_6	3.397(9)	Cl_3 ... C_6	3.527(9)
Cl_1 ... C_1	3.41(1)	Cl_3 ... N_3	3.677(8)
Cl_1 ... N_2	3.452(8)	Cl_3 ... C_4	3.720(9)
Cl_1 ... N_1	3.458(8)	Cl_3 ... C_2	3.77(1)
Cl_1 ... C_5	3.656(9)	Cl_4 ... N_2	3.314(8)
Cl_1 ... C_2	3.70(1)	Cl_4 ... N_3	3.432(7)
Cl_2 ... N_4	3.373(7)	Cl_4 ... C_2	3.64(1)
Cl_2 ... C_3	3.41(1)	Cl_4 ... N_5	3.693(8)
Cl_2 ... N_1	3.486(7)	Cl_3 ... C_3	3.45(1)
Cl_2 ... N_3	3.487(7)		
Cl_2 ... C_4	3.54(1)		
Cl_2 ... C_5	3.86(1)		

Table 5.10

Intramolecular Bond Distances and Angles for the Tetrachlorozincate(II) Anion

π - ISOMER

Intramolecular Bond Distances

Atoms	Distance, Å	Atoms	Distance, Å
$Zn - Cl_1$	2.274(3)	$Zn - Cl_3$	2.242(3)
$Zn - Cl_2$	2.250(3)	$Zn - Cl_4$	2.278(3)

Intramolecular Bond Angles

Atoms	Angle, deg.	Atoms	Angle, deg.
$Cl_1 - Zn - Cl_2$	104.5(1)	$Cl_2 - Zn - Cl_3$	112.1(1)
$Cl_1 - Zn - Cl_3$	113.0(1)	$Cl_2 - Zn - Cl_4$	112.9(1)
$Cl_1 - Zn - Cl_4$	108.1(1)	$Cl_3 - Zn - Cl_4$	106.3(1)

- ISOMER

Intramolecular Bond Distances

Atoms	Distance, Å	Atoms	Distance, Å
$Zn - Cl_1$	2.284(4)	$Zn - Cl_3$	2.256(5)
$Zn - Cl_2$	2.272(5)	$Zn - Cl_4$	2.279(4)

Intramolecular Bond Angles

Atoms	Angle, deg.	Atoms	Angle, deg.
$Cl_1 - Zn - Cl_2$	108.8(2)	$Cl_2 - Zn - Cl_3$	110.5(2)
$Cl_1 - Zn - Cl_3$	107.3(2)	$Cl_2 - Zn - Cl_4$	107.8(2)
$Cl_1 - Zn - Cl_4$	111.0(2)	$Cl_3 - Zn - Cl_4$	111.5(2)

β-[Co(en)(dpt)Cl]$ZnCl_4$[33], 2.26Å in $Na_2ZnCl_4.3H_2O$[110], and 2.287(15)Å in $[N(CH_3)_4]_2[ZnCl_4]$[111].

C H A P T E R 6

OTHER SYSTEMS CONTAINING TRIDENTATE POLYAMINE LIGANDS AND BIDENTATE LIGANDS

EXPERIMENTAL

Analytical data for the complexes are presented in Table 6.1. Infrared spectra in the range 4000-400 cm^{-1} are presented in Fig. 6.3.

Isomer of Chloro(acetyl acetonato)(dipropylenetriamine) cobalt(III) chloride

trans-$Co(dpt)Cl_3$ (3 g) was suspended in water (15 ml) containing NaOH (1 g) and acetylacetone (2 ml, 100%) was added. The solution was warmed at 60° for 30 min. and then 12 F HCl (15 ml) was added. The solution was allowed to stand at room temperature and after three days the purple-brown needle-like crystals that deposited were collected, washed with 2-propanol and then ether. The crude product was recrystallised by dissolving it in 0.2 F CH_3CO_2H at 40° (0.5 g/10 ml) and then adding 12 F HCl (10 ml). The needle-like crystalline product that deposited on cooling the solution in an ice bath was collected, washed and dried as above.

The total yield was 1.32 g or 38.8%.

Isomer of Chloro(dimethylglyoximato)(diethylenetriamine) cobalt(III) chloride

trans-$Co(dien)Cl_3$ (3 g) was suspended in water (30 ml) and dimethylglyoxime (2 g) dissolved in ethanol (30 ml)

Table 6.1

Analytical Data for [Co(acac)(dpt)Cl]Cl and [Co(dmg)(dien)Cl]Cl_2

Complex	Calculated			Found		
	C%	Co%	X%[a]	C%	Co%	X%[a]
[Co(acac)(dpt)Cl]Cl		16.36	19.68		16.19	19.51
[Co(dmg)(dien)Cl]Cl_2	24.99	15.32	27.65	25.12	15.49	26.30

a Total halide as found by Ag^+ titration.

Table 6.2

Visible Absorption Maxima and Minima for $Co(acac)(dpt)Cl^{+}$ and $Co(dmg)(dien)Cl^{2+}$ in Aqueous Solution at 20-25°. [a]

Complex	λ min	λ max	λ min	λ max	λ min	λ max
$Co(acac)(dpt)Cl^{+}$		390sh[b] (130)	465 (23.0)	527 (46.7)		575sh (30.3)
$Co(dmg)(dien)Cl^{2+}$		420sh (196)	487 (65.2)	502 (66.3)		

a Numbers inside parentheses are the molar absorbancy indices, a_M, (extinction coefficients, ε) in $M^{-1}cm^{-1}$ Wavelengths are in nanometers. Spectra are measured in 0.1 F $HClO_4$.

b sh = shoulder.

containing NaOH (2 g) was added. The solution was heated at 70° for 20 min. and then 12 F HCl (40 ml) containing $ZnCl_2$ (5 g) was added. On standing the solution at room temperature for 24 hours the product began to deposit and it was collected in crops, washed with 2-propanol and then ether. The crude product was recrystallised by dissolving each crop in 0.2 F CH_3CO_2H at 60° (0.1 g/45 ml) and then adding 12 F HCl (5 ml/0.1 g) containing $ZnCl_2$ (2.5 g/0.1 g). The orange products that deposited on cooling the solutions to room temperature were collected in fractions, washed and dried as above. The first three crops contain trans-$[Co(dmg)_2Cl_2]$ Cl and free dimethylglyoxime. The yield was 0.50 g or 11.7%.

Discussion

In these two systems, only one isomer has been isolated by the synthetic method employed. It is probable that the $Co(acac)(dpt)Cl^+$ isomeric cation has the geometric configuration IIIa (Fig. 4.1) because the synthetic reaction is performed under strongly basic conditions and the IIIb → IIIa isomerisation of the dpt ligand under these conditions has been established (Chapter 4).

Similarly, the $Co(dmg)(dien)Cl^{2+}$ isomeric cation probably has the geometric configuration I or IIIb, since

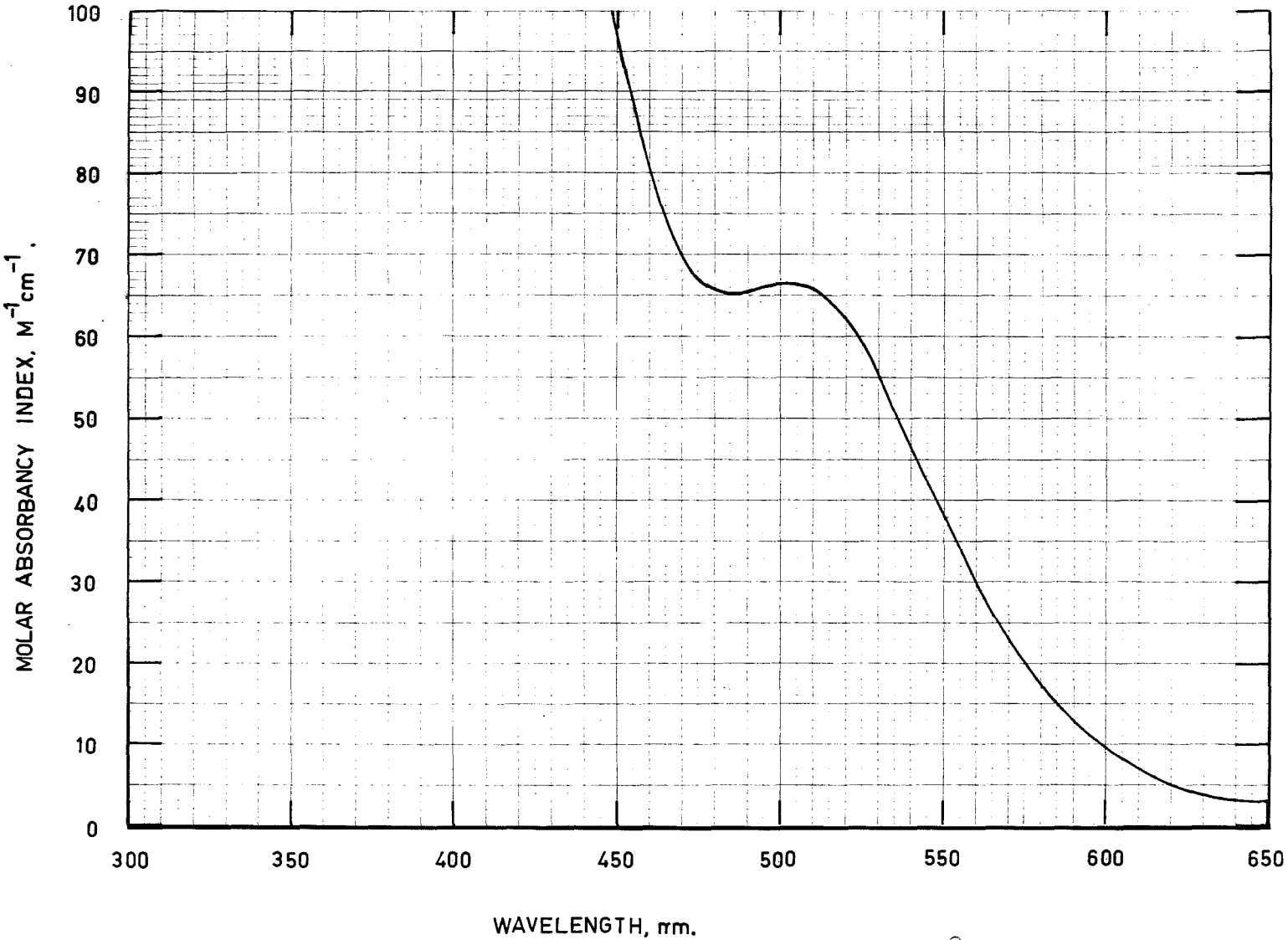


Figure 6.1 Visible absorption spectrum of $Co(dmg)(dien)Cl^{2+}$ in 0.1 F $HClO_4$ at 20-25°.

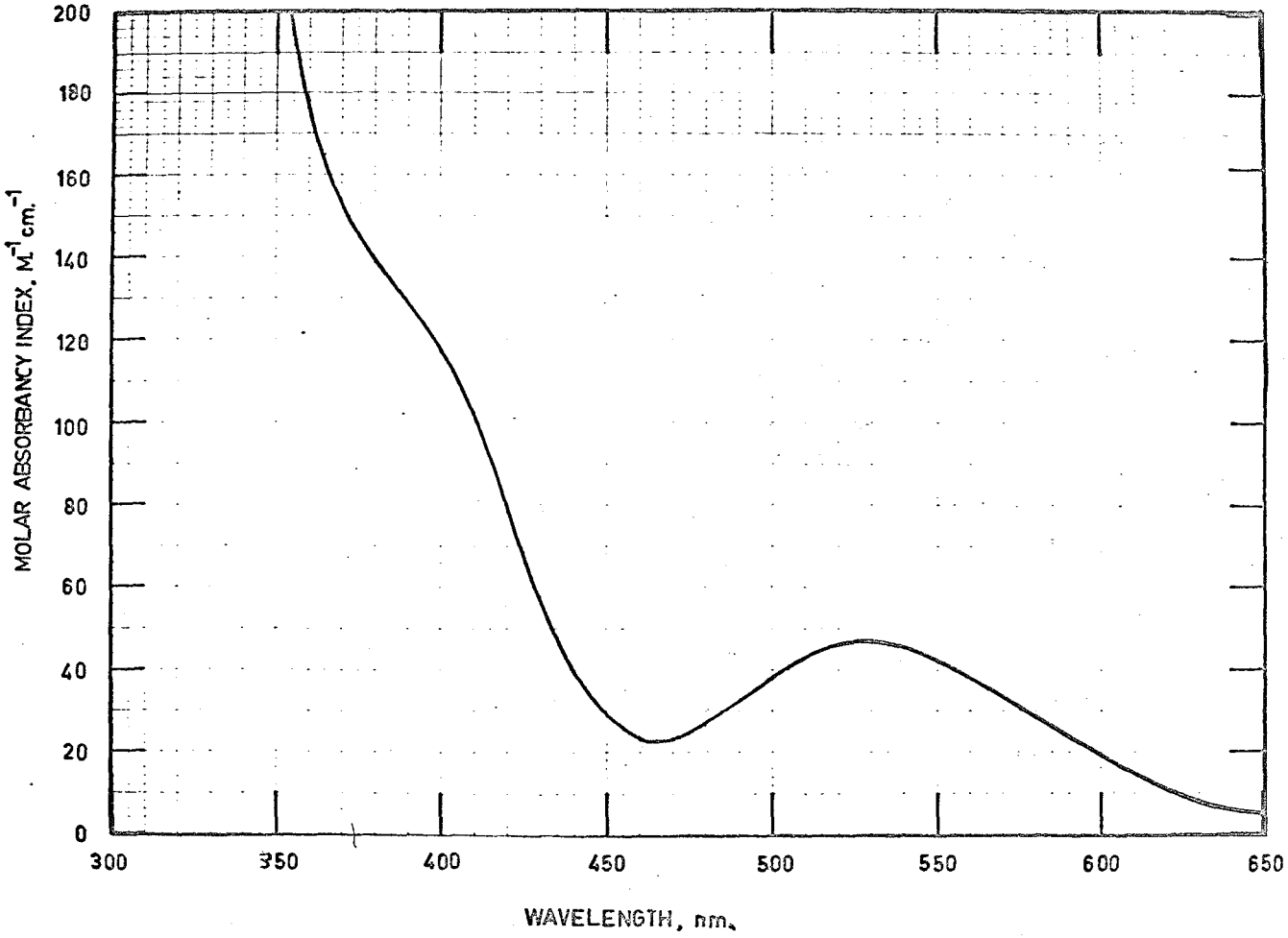
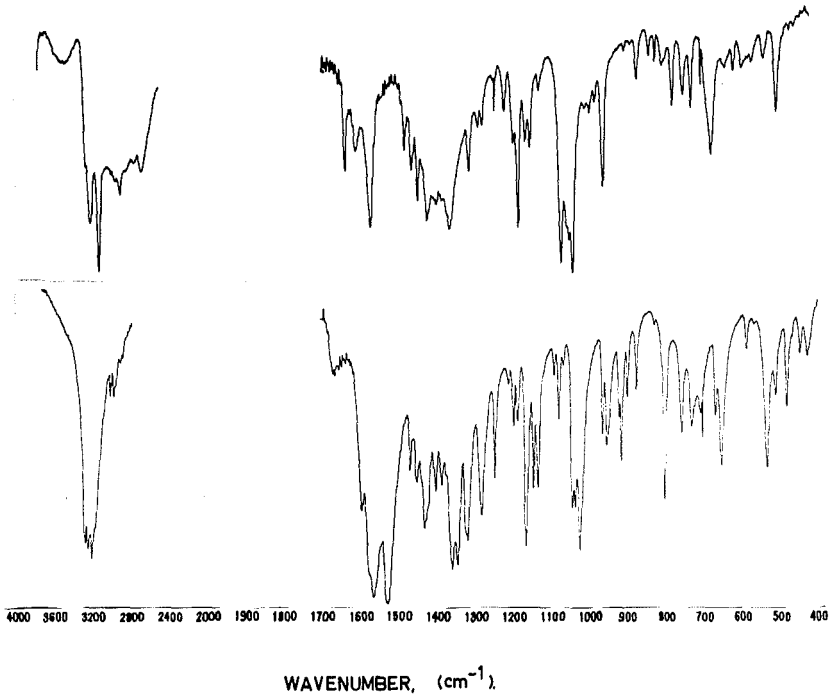


Figure 6.2 Visible absorption spectrum of $Co(acac)(dpt)Cl^{+}$ in 0.1 F $HClO_4$ at 20-25°.

Figure 6.3 Infrared spectra of $[Co(dmg)(dien)Cl]Cl_2$ (top) and $[Co(acac)_2(dpt)Cl]Cl$ (bottom) in the region 4000-400 cm^{-1} (KBr Disc).



the synthesis of this complex is also performed in strongly basic solution. The I - IIIb mixture formation under basic conditions has also been established (Chapter 4).

The visible absorption spectra of these complexes (Fig. 6.1, 6.2) show one maxima at about 500 nm and there are prominent shoulders on the charge-transfer bands in the 400 nm region. The visible absorption maxima and minima (Table 6.2) of $Co(acac)(dpt)Cl^{2+}$ are at longer wavelengths, whereas those of $Co(dmg)(dien)Cl^{2+}$ are at shorter wavelengths than the corresponding diamine analogs. The infrared spectra of these complexes show the absorptions expected for acetylacetonato and dimethylglyoximato ligands superimposed on a typical cobalt(III)-polyamine spectrum (Fig. 6.3.)

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THE SYNTHESIS OF μ-PEROXO AND CHLOROPENTAMINECOBALT(III) COMPLEXES WITH POLYAMINE LIGANDS

A.R. Gainsford and D.A. House

Department of Chemistry, University of Canterbury,

Christchurch, New Zealand.

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A.R. Gainsford and D.A. House

Department of Chemistry, University of Canterbury,

Christchurch, New Zealand.

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A number of chloropentaminecobalt(III) tetrachlorozincate(II) salts (see Table) have been prepared, in several geometric configurations, by reacting the corresponding μ-peroxodicobalt(III) decamine perchlorates with $HCl/ZnCl_2$ solution.

Table

Complex [a,b]	Number of Isomers Isolated		
	Previous work	This work	Theoretical
$[Co(tetren)Cl]ZnCl_4$	2 (1,2,3); 4 (4)	-[c]	4
$[Co(en)(dien)Cl]ZnCl_4$	1 (3); 2 (5)	2	3
$[Co(en)(dpt)Cl]ZnCl_4$		3	3
$[Co(tmd)(dien)Cl]ZnCl_4$		2	3
$[Co(tmd)(dpt)Cl]ZnCl_4$		3	3
$[Co(trien)(NH_3)Cl]ZnCl_4$	1 (3)	3	4
$[Co(dien)(NH_3)_2Cl]ZnCl_4$		2	4

[a] Abbreviations used: tetren = $NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$; trien = $NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$; dien = $NH_2(CH_2)_2NH(CH_2)_2NH_2$; en = $NH_2(CH_2)_2NH_2$; dpt = $NH_2(CH_2)_3NH(CH_2)_3NH_2$; tmd = $NH_2(CH_2)_3NH_2$.

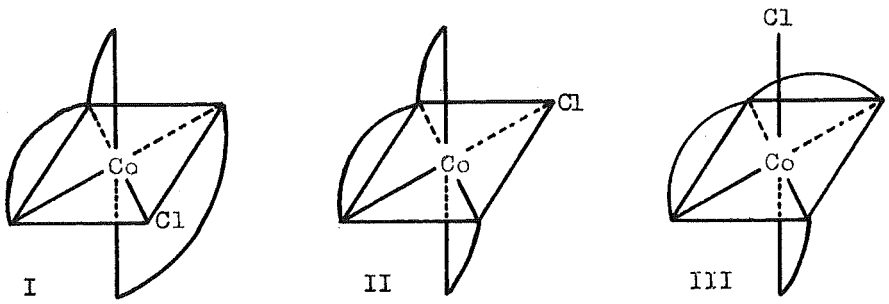
[b] Satisfactory analyses have been obtained for all the isomeric forms listed in this table. Full details of the experimental methods will be reported later.

[c] Not investigated here.

The dark brown polyamine μ-peroxo intermediates were formed by oxidising an aqueous solution of hydrated cobalt(II) nitrate, sodium perchlorate and the polyamine (tetren) or polyamine mixture with molecular oxygen. The required ammine μ-peroxo perchlorate complexes were prepared from $[Co_2(NH_3)_{10}O_2](NO_3)_4 \cdot 2H_2O$ (6) by reaction with an aqueous solution of the polyamine at room temperature, followed by addition of $NaClO_4$.

In the case of $[Co(trien)(NH_3)Cl]ZnCl_4$, for example, the three isomers isolated from the decomposition of $[Co_2(trien)_2(NH_3)_2O_2](ClO_4)_4 \cdot 2H_2O$ with 3.6 F HCl containing $ZnCl_2$, are deposited successively on evaporation of the solution. With $[Co(en)(dpt)Cl]ZnCl_4$, however, only two isomers (α and β) are isolated from the initial decomposition of the μ-peroxo and the third is generated by decomposition of one of the $[Co(en)(dpt)NO_2]ZnCl_4$ isomers formed from the α form (cf. $Co(tetren)Cl^{2+}$, Ref. 1). The geometric isomers of the chloropentamine cobalt(III) complexes listed in the table have been characterised by analysis, infrared and visible absorption spectra and X-ray powder diffraction patterns. Infrared spectral measurements can distinguish about 5% of one isomer in the other (1).

The three possible geometric configurations of a $Co(AA)(ABA)Cl^{2+}$ complex (AA = bidentate polyamine, ABA = tridentate polyamine) are:



with I, II and III related by edgewise displacement of the coordinated chloride ligand (5). Of these isomers, only II is potentially optically active. In addition, conformational isomers may exist, due to the axial or equatorial arrangements of the NH hydrogen in the coordinated secondary amine group. These conformational isomers are not expected to be distinguished by the techniques used here.

It is interesting that for $Co(en)(dien)Cl^{2+}$ and $Co(tmd)(dien)Cl^{2+}$, only two isomers have been isolated, whereas with dpt as the ligand, there are three isomeric forms produced. This, perhaps, implies a greater flexibility in the dpt ligand, a feature observed in other polyamine ligands where the ethylene bridge has been replaced by a propylene bridge (7).

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quinoline-7-sulfonic acid, prepared as described elsewhere[3, 6], was recrystallised twice from distilled water and a pure sample of the potassium salt was made by adding the requisite quantity of KOH (B.D.H.). Spectra were measured using a Hilger-Uvispec Spectrophotometer (Model H 700–380) with 1 cm thermostated cells (±0·1°C). pH measurements were made using a Beckman pH meter (Model H 2). All measurements were made at 25°C.

STABILITY CONSTANT DETERMINATION

Spectrophotometric method.

Acid dissociation constants were obtained by the method of Schwarzenbach[7] in which the spectrum of the ligand is recorded at constant concentration but at different values of pH, pK_A was then calculated using the relationship

$$pK_A = pH + \log_{10}\left\{\frac{(OD_x - OD_B)}{(OD_{BH} - OD_x)}\right\} \quad (1)$$

where OD_B, OD_{BH} and OD_x are the optical densities of the unprotonated, fully protonated and partially protonated ligand respectively, at the wavelength where the difference between OD_B and OD_{BH} is a maximum. pH in the equation represents the pH at which OD_x was measured. The final value of pK_A was the average of several similar determinations at different pH values.

Chelate stability constants were obtained spectrophotometrically by measuring the spectra of solutions of ligand and metal at fixed concentrations but at various values of pH (Fig. 1). The spectra of the free ligand and fully formed complex were also obtained. The degree of formation of the complex was obtained from the relationship

$$\bar{n} = \left\{\frac{(OD_x - OD_L)}{(OD_{ML} - OD_L)}\right\} \quad (2)$$

where OD_x, OD_L and OD_{ML} are respectively the optical densities of the partially formed complex at a measured value of pH, the free ligand and the fully formed complex at the wavelength where the difference betaeen OD_L and OD_{ML} is a maximum. The negative logarithm of the concentration of

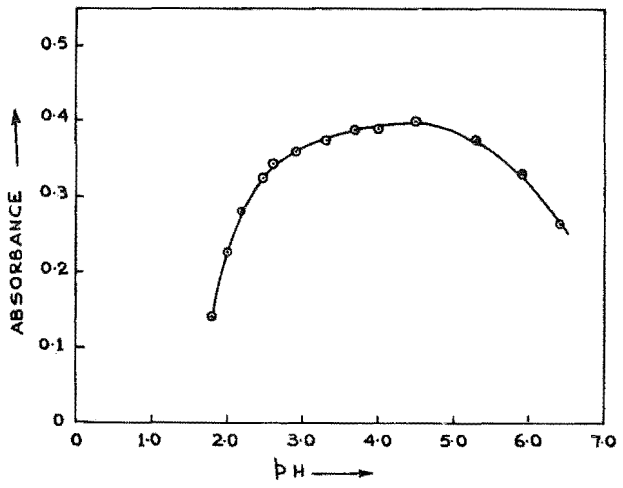

Fig. 1. Variation of absorbance of the Fe (III)–EHQS Chelate with pH. $\lambda_{max} = 610$ nm; $T_M = 1 \times 10^{-3}$ M; $T_L = 2 \times 10^{-3}$ M.

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nonprotonated ligand (pL) was obtained using the Equation [8] (3):-

$$pL = \log_{10}\left\{\frac{(\beta_0^H + \beta_1^H[H] + \beta_2^H[H]^2 + \cdots)}{(T_L - \bar{n}T_M)}\right\} \quad (3)$$

where $\beta_0^H = 1$, β_1^H and β_2^H are the reciprocals of the acid dissociation constants of the ligand, i.e. $[LH]/[L][H]$ and $[LH_2]/[L][H]^2$ respectively. T_L and T_M are the stoichiometric concentrations of the ligand and metal ion. The equation of the formation curve is:-

$$\bar{n} + (\bar{n} - 1) K_1[L] = 0 \quad (4)$$

where $K_1 = [ML]/[M][L]$ is the stability constant.

RESULTS AND DISCUSSION

The ligand and metal ion do not absorb at λ_{max} (= 610 nm) of the complex studied. The values of $\bar{n}$ extend from 0 to 1 indicating that only one complex is formed in the pH range 1·7 to 4·0. The values of K_1 (or β_1) calculated using Equation (4) are shown in the Table.

Table 1. Stability constants for the complex

$T_M = 1{\cdot}0 \times 10^{-3}$ M; $T_L = 2{\cdot}0 \times 10^{-3}$ M; $\lambda_{max} =$ 610 nm; $\log \beta_1^H = 8{\cdot}76$; $\log \beta_2^H = 13{\cdot}03$

S. No.	pH	OD_x	OD_{ML}	$\bar{n}$	pL	$\log \beta_1$
1.	1·80	0·142	0·400	0·3550	12·2152	11·96
2.	2·00	0·225	0·400	0·5625	11·8749	11·98
3.	2·20	0·282	0·400	0·7050	11·5215	11·90
4.	2·45	0·325	0·400	0·8125	11·0621	11·70
5.	2·60	0·345	0·400	0·8625	10·7833	11·58
6.	2·90	0·360	0·400	0·9000	10·2067	11·16
7.	3·30	0·375	0·400	0·9375	9·4466	11·20

Average $\log \beta_1 = 11{\cdot}57 \pm 0{\cdot}41$

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Chemical Laboratories
Birla Institute of Technology and Science
Pilani
Rajasthan, India

C. D. DWIVEDI
S. K. BANERJI

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Trans-triacidotriaminecobalt(III) complexes with tridentate polyamine ligands

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IN AN INVESTIGATION to determine the extent to which increase in ring size influences the stereochemistry of facultative ligands, we have prepared the cobalt(III) complexes, Co(dien)X_3, Co(2,3-tri)X_3 and Co(dpt)X_3 (X = NO_2, Cl, Br, N_3). (Abbreviations used: dien = 2,2-tri = diethylenetriamine = N-(2-aminoethyl)-1, 2-diaminoethane; 2,3-tri = N-(2-aminoethyl)-1,3-propanediamine; dpt = 3,3-tri = dipropylenetriamine = N-(3-aminopropyl)-1,3-diaminopropane.) In this system the chelate ring systems are extended from two 5-membered rings, through one 5 and 6 membered ring, to two 6-membered rings, and for the chloro complexes, the colors are brown, brown and green, respectively.

These complexes can theoretically exist in both facial (*cis*) and peripheral (*trans*) configurations, and id addition, both forms of Co(2,3-tri)X_3 are potentially optically active by virtue of the asymmetric coordinated secondary amine group.

EXPERIMENTAL

Preparation of complexes

$Co(dpt)(NO_2)_3$[1, 2], $Co(dien)(NO_2)_3$[3, 4], $Co(dpt)Cl_3$[1, 2], $Co(dien)Br_3$[5] and $Co(dien)Cl_3$[4, 6] were prepared by the literature methods using the commercial amines. 2,3-tri was obtained from Ames Laboratories and used without further purification. Analytical data for the previously described compounds were in satisfactory agreement with the formula, and data for the previously unreported complexes are presented in Table 1.

Table 1. Analytical data

Complex	Formula	Calculated				Found			
		C	H	N	Co	C	H	N	Co
$Co(dien)Br_3$	$CoC_4H_{13}N_3Br_3$	11·95	3·26	10·46	14·66	12·54	3·30	10·38	14·83
$Co(dien)(N_3)_3$	$CoC_4H_{13}N_{12}$	16·67	4·55	58·33	20·45	17·02	4·60	58·76	20·28
$Co(2,3\text{-tri})Cl_3$	$CoC_5H_{15}N_3Cl_3$	21·26	5·35	14·87	20·86	21·80	5·30	14·27	20·89
$Co(2,3\text{-tri})Br_3$	$CoC_5H_{15}N_3Br_3$	14·44	3·64	10·10	14·17	14·68	3·79	9·84	14·19
$Co(2,3\text{-tri})(N_3)_3$	$CoC\,H_{15}N_{12}$	19·87	5·00	55·62	19·50	19·55	4·80	55·39	19·45
$Co(2,3\text{-tri})(NO_2)_3$	$CoC_5H_{15}N_6O_6$	19·12	4·81	26·75	18·76	19·62	5·11	16·08	18·07
$Co(dpt)Br_3$	$CoC_6H_{17}N_3Br_3$	16·76	3·99	9·77	13·71	17·01	4·21	10·57	13·68

$Co(2,3\text{-tri})X_3$ *complexes*

$Co(2,3\text{-tri})(NO_2)_3$ was prepared from $CoCl_2 . 6H_2O$, $NaNO_2$ and 2,3-tri, using the method of Bosnich and Dwyer[3] for the preparation of $Co(dien)(NO_2)_3$. An 89 per cent yield of the yellow complex was obtained. A sample for analysis was recrystallised from dilute acetic acid. $Co(2,3\text{-tri})Cl_3$ was prepared by heating the trinitro complex in 12 *F* HCl for 30 min. Brown crystals deposited from the cool solution in a 78 per cent yield. These were washed successively with water, 2-propanol and ether.

Triazido complexes. These were prepared from the trichloro complexes using the method of Curtis, Hay and Curtis[2], who prepared $Co(dpt)(N_3)_3$. $Co(dien)(N_3)_3$ and $Co(2,3\text{-tri})(N_3)_3$ are olive green.

Tribromo complexes. $Co(2,3\text{-tri})Br_3$ and $Co(dpt)Br_3$ were prepared from the trichloro complexes by heating them in water and then adding excess 63% HBr solution. The orange salts that deposited were washed with water, 2-propanol and then ether.

Analysis and spectra. C, H and N analyses were made by Dr A. D. Campbell of the University of Otago, New Zealand, and Co was determined spectrophotometrically as previously described[6]. Solid state reflectance spectra were made using a Shimadzu MPS-50L recording spectrophotometer. Solution spectra in DMF were measured in 1 cm matched silica cells using the same instrument.

RESULTS AND DISCUSSION

Of the twelve triacidopolyaminecobalt(III) complexes described here, seven are new compounds and four of these contain the previously unreported ligand N-(2-aminoethyl)-1,3-diaminopropane, 2,3-tri. In this series, the yellow $Co(dien)(NO_2)_3$ has been shown by X-ray crystallography[7] to have the *trans* trinitro configuration, and there is substantial evidence that brown $Co(dien)Cl_3$ also has the *trans* trichloro arrangement[6, 8].

Only the trinitro complexes have any stability in aqueous solution and the other compounds appear to follow $Co(dien)Cl_3$ which hydrolyses to various chloroaquo products in aqueous acid solution[6].

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Table 2. Visible reflectance spectra* of $Co(dien)X_3$, $Co(2,3\text{-tri})X_3$ and $Co(dpt)X_3$ (X = Cl, Br)

$Co(dien)Cl_3$	$Co(2,3\text{-tri})Cl_3$	$Co(dpt)Cl_3$
675 max (670 max)†	680 max	720 max (736 max)‡
605 min (610 min)†	600 min	635 min
535 sh (530 sh)†	535 max	568 max (572 max)‡
	490 min	500 min
470 max (470 max)†	460 sh	450 sh (435 sh)‡
447 m n (450 min)†		
$Co(dien)Br_3$	$Co(2,3\text{-tri})Br_3$	$Co(dpt)Br_3$
720 max (740 max)†	710 max	710 max
652 min (650 min)†	635 min	650 min
510 max (510 max)†	475 max	470 sh
450 min (455 min)†	460 min	

*Wavelengths in nanometers ± 5 nm: sh = shoulder.
†Data in parenthesis from Ref. [5]
‡Data in parenthesis from Ref. [2].

Table 3. Absorption maxima in the visible and u.v. spectra of $Co(dien)X_3$, $Co(2,3\text{-tri})X_3$ and $Co(dpt)X_3$ ($X = NO_2$, N_3)

Complex	Ref.[a],[b]	DMF[a],[c]	H_2O[d]	H_2O[e]
$Co(dien)(NO_2)_3$	240		250	250
	330	345	338	330
	435 sh	435 sh	433	435
$Co(2,3\text{-tri})(NO_2)_3$	240			
	330	346		
	442	438		
			MeOH[f]	
$Co(dpt)(NO_2)_3$	244			
	333	348		
	454, 466[f]	453	452	
	Ref.[a],[b],[g]			
$Co(dien)(N_3)_3$		337		
	510 sh			
	610	575		
$Co(2,3\text{-tri})(N_3)_3$		340		
		550 sh		
	595 br	590		
$Co(dpt)(N_3)_3$		348		
	595, 595[f]	612		
	710, 724[f]			

[a]This work; wavelengths in nanometers ± 5 nm; sh = shoulder; br = broad. [b]Ref. = reflectance spectra. [c]DMF = dimethylformamide, 320–800 nm range. [d]Data from Ref. [4]. [e]Data from A. V. Ablov and E. V. Popa, *Russ. J. inorg. Chem.* **8**, 161 (1963), (Eng. trans.). [f]Data from Ref. [2]. [g]400–800 nm range.

Dimethylformamide (DMF) acts as a solvent for both the trinitro and triazido complexes but solvolysis of the latter may also be extensive as there are considerable difference between the visible reflectance and DMF solution spectra (Table 3).

On the basis of a color comparison, it could be thought that the green $Co(dpt)Cl_3$ may have the *cis* trichloro configuration, especially as *cis*-$Cr(dien)Cl_3$ is also green[5, 6, 8, 9]. However, the reflectance spectra (Fig. 1, Table 2) of the trichloro complexes are all very similar, with only a progressive

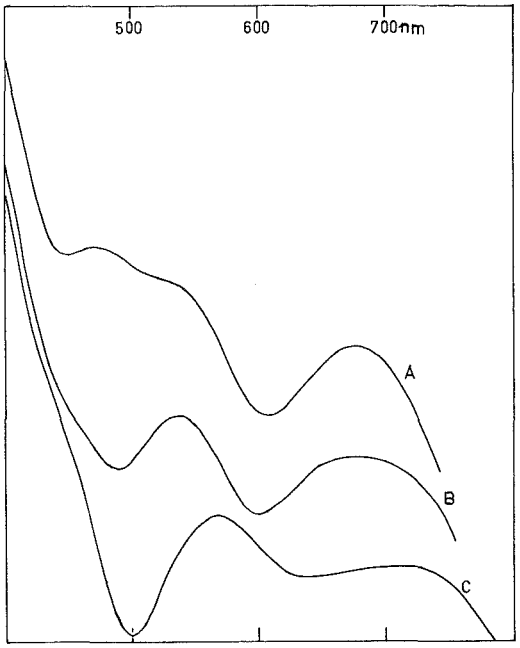

Fig. 1. Solid state reflectance spectra of (A) $Co(dien)Cl_3$, (B) $Co(2,3\text{-tri})Cl_3$ and (C) $Co(dpt)Cl_3$. Wavelengths are in nanometers with an arbitrary intensity scale.

shift to longer wavelengths from dien to dpt, and a similar *trans* configuration is suggested. The red to orange tribromo complexes exhibit similar changes in their reflectance spectra and the yellow trinitro and olive-green triazido complexes also have similar reflectance and solution spectra (Table 3).

It thus appears that this series of polyamine complexes adopts a *trans* configuration for the acido ligands Cl^-, Br^-, NO_2^- and N_3^- regardless of the size of the rings formed by the polyamine. Previous observations on this effect have shown that in the tetramine series, increase in ring size of the polyamine ligand enhances the stability of *trans* diacido complexes[10].

The only reported *cis* complex with three monodentate ligands reported for this series of tridentate polyamines is the *cis*-$Co(dien)(OH_2)_3^{3+}$ cation[6] and work is in progress to establish the configuration of the other triaquo polyamine cations.

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Department of Chemistry
University of Canterbury
Christchurch, New Zealand

A. R. GAINSFORD
D. A. HOUSE

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Chromato and dichromato complexes of cobalt (III)

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IN A RECENT paper[1] on the i.r. spectra of tetrahedral oxyanions as ligands, the characteristic features of the spectra of coordinated chromato group have been described. The ability of the chromate ion to act as a ligand in compounds of Sn[2] and Sb[3] has also been established. Further, the electronic spectra of Co(III) amines including $[Co(NH_3)_5CrO_4]^+$ have been previously reported[4].

The present work was undertaken in order to obtain further information about the chromate ion as a ligand in Co(III) complexes and to compare the reactions of that ion with those of the dichromate ion.

RESULTS AND DISCUSSION

Comber and Griffith[1] have found that the ν_1 mode of the chromate ion is activated in the i.r. on coordination and that it appears at 870–840 cm^{-1}. The ν_3 mode is found at 880 cm^{-1} for the free ion, it is split to a doublet for a C_{3v} (monodentate) and to a triplet for a C_{2v} (bidentate) ligand attachment.

I.R. studies have been previously reported[5] for the dichromate ion.

The i.r. data (Table 2) suggest that the chromate ion acts as a bidentate ligand in the compound $[Co(en)_2CrO_4]Cl$, as the ν_3 band is split in the same way than in $[Co(NH_3)_4CrO_4]NO_3$. The assignment of the chromato bands in $[Co(en)_2CrO_4]_2Cr_2O_7$ was rather difficult because they were masked by those of the dichromate ion, nevertheless the structure of the compound was confirmed by the electronic spectra, as discussed below. The i.r. spectrum of the $Cr_2O_7^=$ in $[Co(NH_3)_5H_2O]_2(Cr_2O_7)_3$ differs from that of $K_2Cr_2O_7$, which is in agreement with the fact that the i.r. spectra of the dichromate ion depends upon the nature of the cation[5] (Table 3).

Table 1. Electronic spectra

Complex	Reflectance spectra ν_1 (cm^{-1})	Aqueous solution (10^{-4} *M*) ν_1 (cm^{-1})*	Aqueous solution (10^{-4} *M*) ν_1 (cm^{-1})†	Ref. [4]
$[Co(NH_3)_5Cl]Cl_2$	18,740	18,920		18,730
$[Co(NH_3)_5CrO_4]Br$	18,400	18,500	18,520	18,530
$[Co(NH_3)_5H_2O]Br_3$	20,370	20,000	20,150	20,530
$[Co(NH_3)_5H_2O]_2(Cr_2O_7)_3$	18,600			
$[Co(NH_3)_4CrO_4]NO_3$	16,000 18,560	16,530 18,560	18,840	
$[Co(en)_2CrO_4]Cl$	16,000 19,130	16,390 19,050	readily decomposes	
$[Co(en)_2CrO_4]_2Cr_2O_7$	15,940 18,630			
Trans-$[Co(NH_3)_4]Cl_2$+				15,900 21,000

*Fresh solutions.

†After 3 hr.

In all cases the ν_2 band is obliterated by charge transfer bands.

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Contribution from the Department of Chemistry, University of Canterbury, Christchurch, New Zealand

Acidopentaminecobalt(III) Complexes with Polyamine Ligands. I. Geometric Isomers of Some Acido(ethylenediamine)-(dipropylenetriamine)cobalt(III) Complexes

A. R. Gainsford and D. A. House

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The three geometric isomers (α, β and γ) of Co(en)-(dpt)Cl²⁺ have been isolated as the $ZnCl_4^{2-}$, $ZnBr_4^{2-}$, $Zn(NCS)_4^{2-}$ and ClO_4^- salts. The α and β forms are prepared by the decomposition of $[Co_2(en)_2(dpt)_2O_2]$-$(ClO_4)_4 . 2H_2O$ in HCl. α–[Co(en)(dpt)Cl]$ZnCl_4$ forms two (β and γ) $Co(en)(dpt)NO_2^{2+}$ isomers, and from these the β and γ–[Co(en)(dpt)Cl]$ZnCl_4$ isomers respectively, can be obtained. Bromo, iodo, azido, isothiocyanato and aquo complexes have also been prepared. The configurations of these isomers are discussed in terms of chemical reactions and infrared and visible spectral considerations.

Introduction

Recent interest in the properties of geometric isomers of Co^{III} complexes formed by different conformations of polyamine ligands[1] *e.g.* tetren[2-6] or trien[7] has prompted us to study several acidopentaminecobalt(III) systems formed with mixed triamine-diamine ligands.

There are potentially three geometric configurations generated by edgewise displacements in a M(AA)-(ABA)X^{2+} system (AA = bidentate linear polyamine, ABA = tridentate linear polyamine) (Figure 1; I, II, and III). In adition, each of these modifications can exist in two conformations, depending whether the hydrogen associated with the coordinated secondary amine of the tridentate polyamine is *cis* or *trans* to the diamine (Figure 1).

Complexes of the acido diamine-triamine type that have previously been reported[2,8-10] are Co(en)(dien)X^{2+} (2 isomers[9,10]) Co(pn)(dien)X^{2+} (1 isomer[8]) and Co-(tmd)(dien)$^{2+}$ (1 isomer[8]) .These were all prepared by reacting a trinitrotriaminecobalt(III) complex with another polyamine.[2,8-10]

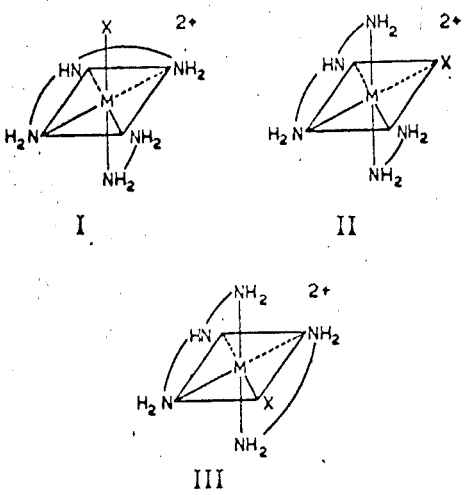

Figure 1. Possible geometric isomers of M(AA)(ABA)X^{2+} (AA = bidentate linear polyamine, ABA = tridentate linear polyamine).

Using a different synthetic method for mixed polyamine systems,[11] we have isolated Co(en)(dien)X^{2+} (4 isomers), Co(pn)(dien)X^{2+} (3 isomers), Co(ibn)(dien)-X^{2+} (1 isomer), Co(tmd)(dien)X^{2+} (2 isomers), Co-(en)(dpt)X^{2+} (3 isomers), Co(pn)(dpt)X^{2+} (2 isomers) and Co(tmd)(dpt)$^{2+}$ (3 isomers).

We describe here the preparation, properties, reactions and geometric configurations of the three isomers isolated for the Co(en)(dpt)X^{n+} system.

Two (α and β) (probably configurations II and I respectively) of the three chloro isomers are isolated as the tetrachlorozincate(II) salts when $[Co_2(en)_2-(dpt)_2O_2](ClO_4)_4 . 2H_2O$ is reacted with HCl containing $ZnCl_2$ and the third chloro isomer (γ) (probably configuration III) is generated by the HCl/$ZnCl_2$ decomposition of a nitro complex derived from the α isomer. The isomers have been distinguished on the basis of infrared and visible absorption spectra and by their X-ray powder diffraction patterns. These methods are not, however, expected to differentiate between the different conformations due to the NH proton.

(1) Abbreviations used: en = $NH_2(CH_2)_2NH_2$, pn = $NH_2CH(CH_3)CH_2NH_2$, tmd = $NH_2(CH_2)_3NH_2$, ibn = $NH_2C(CH_3)_2CH_2NH_2$, dien = $NH_2(CH_2)_2NH(CH_2)_2NH_2$, dpt = $NH_2(CH_2)_3NH(CH_2)_3NH_2$, trien = $NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$ and tetren = $NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$

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Table I. Analitical data

Complex	Calculated					Found				
	C%	H%	N%	Co%	X% [a]	C%	H%	N%	Co%	X% [a]
$[Co_2(en)_2(dpt)_2O_2](ClO_4)_4 2H_2O$	19.88	5.61	14.50	12.20	—	19.99	5.83	13.88	12.22	—
$[Co(en)(dpt)Cl]ZnCl_4$—α	19.49	5.11	14.29	11.96	35.96	19.56	5.20	14.19	11.86	35.81
—β						19.51	5.10	14.03	12.11	36.02
—γ						19.50	5.06	14.43	12.05	36.01
$[Co(en)(dpt)Cl](ClO_4)_2$—α	19.83	5.21	14.43	12.17	7.36	20.27	5.50	13.97	12.11	7.45
—β						20.17	5.55	13.93	12.07	7.41
—γ						19.86	5.33	14.68	12.05	7.45
$[Co(en)(dpt)Cl]Zn(NCS)_4$—α	24.71	4.32	21.61	10.10	45.89	24.76	4.87	21.37	10.20	45.82
—β						24.37	4.89	21.67	10.22	45.37
—γ						23.78	4.68	20.32	10.05	45.49
$[Co(en)(dpt)Cl]ZnBr_4$—α	14.32	3.76	10.44	8.79	52.95	15.08	3.95	10.73	8.75	52.91
—β						14.77	3.94	10.27	8.62	52.69
—γ						14.50	3.91	10.85	8.67	52.61
$[Co(en)(dpt)Cl]ZnI_4$—α				6.86	62.34				6.77	63.11
$[Co(en)(dpt)Br]ZnBr_4$—α	13.27	3.48	9.68	8.13	55.12	13.59	3.54	9.62	8.11	55.34
—β						13.77	3.68	9.48	8.07	55.27
—γ						13.64	3.58	9.39	8.17	55.19
$[Co(en)(dpt)Br](ClO_4)_2$—α	17.63	4.26	12.85	10.81	14.66	18.98	5.18	13.10	10.83	14.59
—γ									10.81	14.63
$[Co(en)(dpt)Br]Br_2$—α	19.61	5.14	14.29	12.03	48.93	19.00	5.29	14.07	11.98	48.87
$[Co(en)(dpt)Br]ZnCl_4$—α	17.88	4.69	13.03	10.79	41.28	18.55	4.97	12.84	10.89	41.28
—γ									10.81	41.16
$[Co(en)(dpt)Br]Zn(NCS)_4$—α	22.98	4.01	20.07	9.38	49.71	23.39	4.22	20.26	9.24	49.38
—γ									9.38	49.54
$[Co(en)(dpt)I]I_2$—α				9.34	60.34				9.24	60.31
—β									9.25	60.27
—γ									9.27	60.45
$[Co(en)(dpt)I](ClO_4)_2$—α	16.68	4.37		10.23	22.03	16.61	4.28		10.11	21.97
$[Co(en)(dpt)I]ZnCl_4$—α				10.08	45.99				10.05	45.89
$[Co(en)(dpt)I]Zn(NCS)_4$—α				8.73	53.19				8.68	53.36
$[Co(en)(dpt)I]ZnBr_4$—α				7.73	58.59				7.70	58.53
$[Co(en)(dpt)NO_2]ZnCl_4$—β	19.08	5.00	16.69	11.70	28.16	19.02	5.04	16.43	11.54	28.28
—γ						19.05	4.99	16.22	11.73	28.21
$[Co(en)(dpt)NO_2](ClO_4)_2$—β	19.40	5.08	16.98	11.88	—	19.11	5.21	17.31	11.72	—
—γ						19.47	5.15	17.78	11.92	—
$[Co(en)(dpt)NO_2]Zn(NCS)_4$—γ	24.10	4.21	23.43	9.86	38.85	25.05	4.68		9.91	38.78
$[Co(en)(dpt)NO_2]ZnBr_4$—γ				8.65	46.92				8.55	46.99
$[Co(en)(dpt)(NCS)]Zn(NCS)_4$—β	25.75	4.16	23.11	9.72	47.89	26.50	4.89	22.57	9.65	48.04
—γ									9.65	47.80
$[Co(en)(dpt)(NCS)]ZnCl_4$—β				12.04	40.83				12.01	40.74
$[Co(en)(dpt)N_3]ZnCl_4$—α				11.80	28.39				11.72	28.56
$[Co(en)(dpt)N_3](ClO_4)_2$—α				11.62	—				11.51	—
$[Co(en)(dpt)N_3]ZnBr_4$—α				8.70	47.20				8.69	47.23
$[Co(en)(dpt)N_3]Zn(NCS)_4$—α				9.99	39.58				9.82	39.29
$[Co(en)(dpt)(OH_2)](ClO_4)_2$—α				10.40	—				10.22	—

[a] Total halogen or NCS^- as found by Ag^+ titration.

Experimental Section

The commercial amines were used without further purification. All other chemicals were reagent grade. Analytical data are listed in Table I.

μ-Peroxobis(ethylenediamine)bis(dipropylenetriamine)dicobalt(III) Perchlorate Dihydrate: An aqueuos solution (200 ml) of ethylenediamine (6 g) and dipropylenetriamine (13.1 g) was added to a stirred solution of $Co(NO_3)_2 . 6H_2O$ (29 g) and $NaClO_4 . H_2O$ (30 g) in 500 ml of water. A rapid stream of O_2 gas was passed through the stirred, room temperature solution and after two hr the brown crystals that deposited were collected, washed with 2-propanol ,then ether and finally air dried . The yield was 37 g or 45%.

A sample for analysis was prepared by dissolving 2 g of the crude material in the minimum volume (75 ml) of room temperature water. Excess solid $NaClO_4 . H_2O$ was added to the stirred solution and the brown crystalline product that deposited was collected, washed and dried as above. An 82% recovery was obtained.

α and β-Chloro(ethylenediamine)(dipropylenetriamine)cobalt(III) Tetrachlorozincate(II): The crude $[Co_2(en)_2(dpt)_2O_2](ClO_4)_4 . 2H_2O$ prepared above (30 g) was added to a solution of 85 ml of 12 F HCl and 170 ml of water containing 50 g of $ZnCl_2$. The mixture was heated on a steam bath (ca. 80°) until the effervescence ceased (*ca.* 45 min). During this time the mauve-pink crude α isomer deposited. The cooled solution was filtered through sintered glass and the product (14 g, 75%) was washed with 2-propanol and then ether.

The aqueous mother liquor was evaporated to about 200 ml on a steam bath and then allowed to stand at room temperature for two days. About 2 g (10% yeild) of violet crystals (β isomer) were obtained.

The impure α isomer was recrystallised by dissolving it in the minimum volume (ca. 250 ml) of 80° 0.2 F HCl and adding 50 ml of 6 F HCl together with

25 g of $ZnCl_2$. The pure α isomer commenced to crystallise from the hot solution and after cooling to room temperature in an ice bath, was collected and washed as above. Recrystallisation of the β isomer was effected similarly but with a corresponding reduction in volumes and weights of reagents. Losses on recrystallisation were mechanical.

The effect of the HCl concentration on the yield was determined by adding 2 g of $[Co_2(en)_2(dpt)_2O_2](ClO_4)_4 . 2H_2O$ to solutions of HCl (16.6 ml) containing 3.3 g of $ZnCl_2$ and heating at 80° for 30 min.

The product was filtered from the cooled solution, washed and dried as above and weighed. Results are presented in the order, acid strength (F), (weigth of α-[Co(en)(dpt)Cl]$ZnCl_4$ obtained): 7.2 (0.53 g), 6.0 (0.57 g), 4.8 (0.57 g), 3.6 (1.01 g), 2.4 (0.75 g), 1.2 (0.33 g). There was incomplete reaction with 1.2 F HCl and with 7.2 F HCl, much $CoCl_4^{2-}$ was formed.

γ-Nitro(ethyenediamine)(dipropylenetriamine)cobalt(III) Tetrachlorozincate(II): Two grams of α-[Co(en)(dpt)Cl]$ZnCl_4$ was dissolved in 50 ml of 0.2 F HCl and 6 g of $NaNO_2$ added. The solution was heated at 80° for 30 min. Mild effervescence occurred and the color changed from red to orange-yellow. The hot solution was slowly poured into a hot solution of 5 g of $ZnCl_2$ in 200 ml. of 50/50 acetone/2-propanol solution. The yellow crystals that deposited on cooling were collected on sintered glass and washed with acetone and ether: yield 60%.

The mother liquor from this synthesis slowly deposited orange-red crystals of β-[Co(en)(dpt)NO_2]$ZnCl_4$ (see below) as the acetone evaporated.

The crude γ-nitro (1.2 g) was recrystallised by dissolving it in the minimum volume of 0.2 F HCl and adding this to 100 ml of acetone. Yellow crystal spangles (75% recovery) were slowly deposited and were collected and washed as above.

β-Nitro (ethylenediamine) (dipropylenetriamine) cobalt(III) Tetrachlorozincate(II): Similar reaction conditions were used as for the synthesis of the γ-nitro isomer except that β-[Co(en)(dpt)Cl]$ZnCl_4$ was used. The orange crystals that deposited from the aqueous acetone/2-propanol solution, after two days, were washed with 2-propanol and then ether; yield 75%.

This isomer is soluble in acetone and was recrystallised as for the γ form but using 2- propanol.

γ-Chloro(ethylenediamine)(dipropylenetriamine)cobalt(III) Tetrachlorozincate(II): One gram of γ-[Co(en)(dpt)NO_2]$ZnCl_4$ was dissolved in 10 ml of hot water and 20 ml of 12 F HCl added. The solution was heated at 80° until a wine red color (about 30 min) and then 5 g of $ZnCl_2$ was added. The heating was continued and the product commenced to crystallise from the hot solution. After cooling, the crystals were collected on sintered glass, washed with 2-propanol and then ether. The yield was 0.6 g or 55%.

α, β and γ-Chloro(ethylenediamine)(dipropylenetriamine)cobalt(III) Perchlorate: The α, β and γ isomers of [Co(en)(dpt)Cl]$ZnCl_4$ were separately dissolved in the minimum volume of 60° 3 F $HClO_4$ and ten times the weight of $NaClO_4 . H_2O$ added. The mauve-red, pale purple and pale red, respectively, perchlorate salts that crystallised on cooling in an ice bath, were washed with 2-propanol, ether and air dried. The yields were α 85%, β 45% and γ 60%.

α, β and γ - Chloro(ethylenediamine)(dipropylenetriamine)cobalt(III) Tetrathiocyanatozincate(II): The α, β and γ isomers of [Co(en)(dpt)Cl]$ZnCl_4$ were separately dissolved in 80° 0.2 F acetic acid (1 g/ 150 ml, 1 g/ 50 ml and 1 g/ 40 ml respectively) and a solution of 3 g of NH_4NCS in 10 ml of water was added. The mauve, purple and red, respectively, tetrathiocyanatozincate(II) salts crystallised immediately. The products were filtered from the well cooled solutions and washed with 5 ml of ice water. The α isomer was also washed with 95% ethanol but the β and γ isomers form oils with this reagent. The yields were α 92%, β 60% and γ 73%.

α, β and γ - Chloro(ethylenediamine)(dipropylenetriamine)Cobalt(III) Tetrabromozincate(II): The α, β and γ isomers of [Co(en)(dpt)Cl]$ZnCl_4$ (2 g, 0.5 g and 0.5 g respectively) were separately dissolved in 80° HCl (50 ml 0.2 F, 15 ml 0.05 F and 15 ml 0.05 F) and 63% HBr (25 ml, 15 ml, and 15 ml) containing $ZnBr_2$ (5 g, 3 g and 3 g) was added. Mauve, purple and red products crystallised immediately. The products were filtered from the well cooled solutions and washed with 2-propanol and ether. The yields were α 97%, β 82% and γ92%.

α-Chloro(ethylenediamine)(dipropylenetriamine)cobalt(III) Tetraiodozincate(II): One half gram of α-[Co(en)(dpt)Cl]$ZnCl_4$ was dissolved in 50 ml of 80° 0.2 F CH_3CO_2H and 1 g of $Zn(ClO_4)_2$ and 5 g of NaI were added. The violet needles that deposited from the ice cooled solution were washed with 2-propanol and recrystallised from 50 ml of 0.2 F CH_3CO_2H by addition of NaI (5 g); yield 60%.

α, β, and γ-Bromo(ethylenediamine)(dipropylenetriamine)cobalt(III) Tetrabromozincate(II): *α-Isomer*. $[Co_2(en)_2(dpt)_2O_2](ClO_4)_4 . 2H_2O$ (6 g) was added to a solution of 16.6 ml of 48% HBr in 33.3 ml of water containing 10 g of $ZnBr_2$. Effervescence occurred and some bromine was evolved. The mixture was heated on a steam bath at 80°, until the effervescence ceased (about 30 min), during which time the purple crystalline product deposited. This was collected on sintered glass and washed sucessively with 50/50 2-propanol/water, 2-propanol and ether; yield 91%.

β-Isomer: One gram of β-[Co(en)(dpt)Cl]$ZnCl_4$ was dissolved in 25 ml of water and 1.2 g of Ag_2O added. The mixture was warmed to 60° for 15 min. and then filtered. A solution of 5 g of $ZnBr_2$ in 10 ml of 48% HBr was added to the hot solution and the crystalline product deposited on cooling; yield 40%

γ-Isomer: One half gram of γ-[Co(en)(dpt)NO_2]$ZnCl_4$ was dissolved in 10 ml of water and 15 ml of 63% HBr added. The solution was heated at 80° for 2 hr and then $ZnBr_2$ (3 g) was added. Shining purple crystals (0.31 g, 65%)were deposited when the solution was cooled in an ice bath.

α and γ-Bromo(ethylenediamine)(dipropylenetriamine)cobalt(III) Perchlorate: One half gram of α or γ-

[Co(en)(dpt)Br]$ZnBr_4$ were separately dissolved in 80° 3 F $HClO_4$ (20 ml) and $NaClO_4 . H_2O$ (5 g) was added. The purple-red perchlorate salts that crystallised on cooling were collected and recrystallised from 3 F $HClO_4$ by the addition of excess $NaClO_4 . H_2O$; yields, α 95%; γ 90%.

α-Bromo(ethylenediamine)(dipropylenetriamine)cobalt(III) Bromide: Six grams of $[Co_2(en)_4(O_2)](ClO_4)_4 . 2H_2O$ was added to 25 ml of 63% HBr in 25 ml of water. The brown tribromide salt (75%) precipitated, after evolution of oxygen and bromine. This material is unstable in air and decomposes to the purple bromide salt. The pure bromide salt (17%) crystallised slowly from the mother liquor and, after filtration, was washed with acetone.

α and γ-Bromo(ethylenediamine)(dipropylenetriamine)cobalt(III) Tetrachlorozincate(II): Two grams of α-[Co(en)(dpt)Br]$ZnBr_4$ was dissolved in 80 ml of 0.1 F HBr and a solution of $ZnCl_2$ (10 g) in 8 F HCl (40 ml) was added. The microcrystalline purple product crystallised immediately and, after filtration, was washed with 2-propanol and ether; yield 88%.

The γ tetrachlorozincate salt was similarly prepared from γ-[Co(en)(dpt)Br]$ZnBr_4$ in an 85% yield.

α and γ-Bromo(ethylenediamine)(dipropylenetriamine)cobalt(III) Tetrathiocyanatozincate(II): One gram of α-[Co(en)(dpt)Br]$ZnBr_4$ was dissolved in 100 ml of 0.2 F CH_3COOH at room temperature and a solution of 3 g of NH_4SCN in 10 ml of water was added. The pale purple product deposited immediately and after filtration from the ice cooled solution, was washed with 5 ml of ice water and air dried; yield 85%.

The γ tetrathiocyanatozincate salt was prepared similarly from γ-[Co(en)(dpt)Br]$ZnBr_4$ in a 95% yield. These compounds form oils with 95% ethanol and ether and turn brown on standing in air.

α, β and γ-Iodo(ethylenediamine)(dipropylenetriamine) cobalt(III) Iodide: Solutions of 2 g of the isomerically pure chloro perchlorate salts in 30 ml of water containing 4 g of NaI were reluxed for 30 min. The olive green iodo iodide salts slowly deposited from the cooled solutions (yellow) on addition of 10 g of NaI. These were collected, washed with 50% aqueous ethanol and then acetone. The yields were: α 75%, β 30%, and γ 25%.

α-Iodo(ethylenediamine)(dipropylenetriamine)cobalt(III) Perchlorate, Tetrachlorozincate(II), Tetrabromozincate(II) and Tetrathiocyanatozincate(II): These salts were prepared by dissolving α-[Co(en)(dpt)I]I_2 in water and adding an excess of the appropriate anion. Data are presented in the order: weight of α-[Co(en)(dpt)I]I_2, volume of water, weight or volume of precipitating agent, yield. 1 g, 50 ml, 10 g $NaClO_4$, 65%. 0.2 g, 40 ml, 2 g $ZnCl_2$ in 20 ml 12 F HCl, 65%. 0.2 g, 30 ml, 2 g $ZnBr_2$ in 10 ml 63% HBr, 60%. 0.25 g, 50 ml, 1.5 g NH_4SCN and 0.5 g $Zn(ClO_4)_2$ in 10 ml water, 50%.

The green salts that were deposited were washed with 2-propanol and ether and air dried.

α-Azido(ethylenediamine)(dipropylenetriamine)cobalt(III) Tetrachlorozincate(II): One gram of α-[Co(en)(dpt)Cl]$ZnCl_4$ was dissolved in 0.2 F CH_3COOH (20 ml) containing NaN_3 (3 g.). As the solution was heated at 80° for 15-20 min the color changed to dark red. The solution was cooled to room tempreature and 100 ml of 1:1 2-propanol-methanol containing 5 of $ZnCl_2$ was added. The red crystalline product that deposited was collected after 24 hr. More product was obtained from the mother liquor on the addition of 20 ml of 2-propanol containing 2 g of $ZnCl_2$. The total yield was 50%.

If $ZnCl_2$ is not added in the above synthesis, a green, water insoluble product (probably Co(dpt)$(N_3)_3$) is slowly deposited.

α-Azido(ethylenediamine)(dipropylenetriamine)cobalt(III) Perchlorate, Tetrabromozincate(II) and Tetrabromozincate(II) and Tetrathiocyanatozincate(II); These salts were prepared by dissolving α-[Co(en)(dpt)N_3]$ZnCl_4$ in dilute acid and adding an excess of the precipitating anion. Data are presented in the order: weight of α-[Co(en)(dpt)N_3]$ZnCl_4$, volume of acid, weight or volume of the appropriate anion, yield. 0.5 g, 10 ml 0.2 F $HClO_4$, 5 g $NaClO_4$, 30%. 0.25 g, 20 ml 0.2 F CH_3CO_2H, 2.5 g $ZnBr_2$ in 10 ml 63% HBr, 75%. 0.25 g, 20 ml 0.2 F CH_3CO_2H, 2.5 g NH_4SCN in 5 ml water, 65%.

The deep purple salts that deposited (slowly in the case of the perchlorate) were washed with 2-propanol and ether and air dried. The $Zn(NCS)_4^{2-}$ salt was washed with ice water only as this forms oils in organic solvents.

β-Isothiocyanato(ethylenediamine)(dipropylenetriamine)cobalt(III) Tetrathiocyanatozincate(II): One and a half grams of α-[Co(en)(dpt)Cl]$ZnCl_4$ was dissolved in 180 ml of water and 20 ml of 2 F NaOH was added. The solution was warmed at 80° for 10 min to hydrolyse the chloro ligand completely and was then made acid (pH 5) by the dropwise addition of glacial acetic acid. A solution of 5 g of NH_4SCN in 20 ml of water was then added and the reaction mixture was allowed to stand to anate. Sparingly water soluble deep red-violet crystal clusters separated after 2 weeks. The product was washed with 3×10 ml portions of ice water and then with 2-propanol, and then air dried; yield 55%.

The product was found to be an isomeric mixture of the α and β forms. Recrystallisation from boiling water produced the isomerically pure β form with a 75% recovery.

β-Isothiocyanato(ethylenediamine)(dipropylenetriamine)cobalt(III) Tetrachlorozincate(II): One half gram of β-[Co(en)(dpt)NCS]$Zn(NCS)_4$ was dissolved in 20 ml of 0.1 F HCl at 80° and the hot solution poured into 100 ml of 2-propanol containing 2.5 g $ZnCl_2$. The red crystals that deposited after two days at room temperature were collected, washed with 2-propanol and air dried; yield 25%.

γ-Isothiocyanato(ethylenediamine)(dipropylenetriamine)cobalt(III) Tetrathiocyanatozincate(II): A suspension of 0.25 g γ-[Co(en)(dpt)NO_2]$ZnCl_4$, 1 g $Zn(ClO_4)_2$ and 3 g NH_4SCN in 30 ml of 1.5 F $HClO_4$ was heated at 80° for 1 hr to form a clear orange solution. The yellow-orange product that deposited

on cooling was recrystallised from hot water and washed with 2-propanol; yield 55%.

β-Nitro(ethylenediamine)(dipropylenetriamine)cobalt(III) Perchlorate: One gram of β-[Co(en)(dpt)Cl]-$ZnCl_4$ was dissolved in 20 ml of 0.2 F $HClO_4$ and 3 g of $NaNO_2$ added. The solution was heated at 80° for 15 min and the color changed from red to orange-red. The hot solution was slowly poured into 50 ml of 50/50 2-propanol/acetone containing 10 g of $NaClO_4 . H_2O$. The orange crystals that deposited after five days were collected and washed with ether; yield 55%. No γ-isomer was detected in this synthesis.

γ-Nitro(ethylenediamine)(dipropylenetriamine)cobalt(III) Perchlorate: Two grams of α-[Co(en)(dpt)-Cl]$ZnCl_4$ was dissolved in 50 ml of 0.2 F HCl, 6 g of $NaNO_2$ was added and the solution heated at 80° for 30 min. Five grams of $NaClO_4 . H_2O$ was added to the hot orange-yellow solution and heating was continued for a further 30 min. The solution was then poured into 200 ml of 1:1 2-propanol/acetone containing 1 ml 70% $HClO_4$, but evaporation to 50 ml was required before orange plates deposited. The product was filtered on sintered glass and washed with acetone and ether; yield 60%.

γ-Nitro(ethylenediamine)(dipropylenetriamine)cobalt(III) Tetrabromozincate(II): One quarter gram of γ-[Co(en)(dpt)NO_2]$ZnCl_4$ was dissolved in 10 ml. 0.2 F CH_3CO_2H and a solution of 2 g of $ZnBr_2$ in 5 ml of 63% HBr was added. The pale yellow product slowly deposited from the ice cooled solution and was washed with acetone and ether; yield 90%.

γ-Nitro(ethylenediamine)(dipropylenetriamine)cobalt(III) Tetrathiocyanatozincate(II): One half gram of γ-[Co(en)(dpt)NO_2]$ZnCl_4$ was dissolved in 50 ml of 80° 0.2 F CH_3COOH and a solution of NH_4SCN (4 g) in 5 ml of water was added. Crystallisation was effected by adding $Zn(ClO_4)_2$ (2 g) and NH_4SCN (4 g) in 10 ml of water to the cooled solution. Yellow spangles were slowly deposited on further cooling in an ice bath. The product was filtered and washed with ether; yield 65%.

α-Aquo(ethylenediamine)(dipropylenetriamine)cobalt(III) Perchlorate: Two grams of α-[Co(en)-(dpt)Cl]$ZnCl_4$ and 2.4 g of Ag_2O were suspended in 50 ml of water and the mixture heated at 60° for 15 min. Sodium perchlorate (8 g) was added to the cooled, filtered solution and this was made acid (pH 2) by dropwise addition of 3 F $HClO_4$. The orange-red solution was evaporated at room temperature with an air stream to about 10 ml and after five days orange crystals were deposited. These were collected, washed with methanol and air dried; yield 25%.

Spectral Measurements: The visible absorption spectra were obtained with a Cary Model 14 recording spectrophotometer. Data for the molar absorbancy indices were obtained in 0.1 F $HClO_4$ at 20-25° using matched 1 cm quartz cell with 0.1 F $HClO_4$ in the reference path. Spectrophotometric analyses for Co were performed using a Beckman DBG recording spectrophotometer. The infrared spectra were determined in both mulls and KBr discs using a Perkin Elmer 337 infrared spectrophotometer. The X-ray powder diffraction patterns were obtained using a Phillips Model PW 1050/25 wide range goniometer connected to a Phillips (PR 2500) one line recorder.

Chemical Analyses: Co was determined by decomposing the complexes with ammonium peroxodisulfate and estimating the Co(II) spectrophotometrically at 620 mμ as the thiocyanate complex in aqueous acetone. Halogen and thiocyanate were determined by potentiometric titration with standard $AgNO_3$ using a Radiometer pH meter. The complexes were decomposed with ammonium peroxodisulfate and acidified with HNO_3 prior to titration. C, H and N analyses were performed by Dr A. D. Campbell of the University of Otago, New Zealand.

Results

Forty-five new $[Co(en)(dpt)X]Z_n$ complexes have been synthesised and of these, the chloro, bromo and iodo salts have been isolated in three isomeric forms (α, β and γ), the isothiocyanato and nitro salts in two forms (β and γ), and the azido and aquo salts in one (α) form. The different isomers are thought to result from different geometric arrangements of the polyamines about the central cobalt(III) atom (Figure 1).

These complexes exhibit colors typical of cobalt(III) pentamine complexes *viz.* the chloro and bromo isomers have various shades of mauve to violet, the iodo isomers are green, the isothiocyanato and nitro isomers are yellow or orange, the aquo complex is orange and the azido salts are dark violet. Maxima and minima in the visible absorption spectra of the $Co(en)(dpt)X^{n+}$ cations in solution are given in Table II, together with those reported earlier for the related $Co(NH_3)_5X^{n+}$ and $Co(tetren)X^{n+}$ cations. Molar absorbancy index vs. wavelength plots for the α, β and γ chloro complexes are presented in Figure 2.

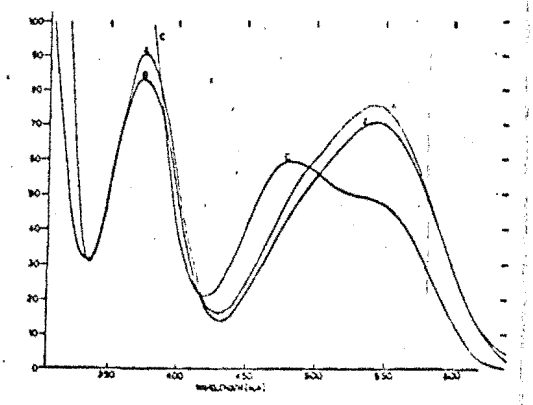

Figure 2. Visible absorption spectra of α, β and γ-Co(en)-(dpt)Cl^{2+} in 0.1 F $HClO_4$ at 20-25°. Ordinate is molar absorbancy index, $M^{-1}cm^{-1}$. A = α isomer, B = β isomer, C = γ isomer.

There are some differences in the visible absorption spectra of the three isomeric $Co(en)(dpt)X^{2+}$ (X = Cl, Br) cations (Table II, Figure 2) and this has been one

Table II. Visible Absorption Maxima and Minima of α, β and γ-Co(en)(dpt)X^{n+}, α and β-Co(tetren)X^{n+} and $Co(NH_3)_5X^{n+}$ in Aqueous Solution at 20-25° [a].

Complex	λ_{max}	λ_{min}	λ_{max}	λ_{min}	λ_{max}	λ_{min}
α-Co(en)(dpt)Cl^{2+} [b]	542(75.1)		517(60.1) sh	431(13.0)	374(90.1)	337(30.8)
β-Co(en)(dpt)Cl^{2+} [b]	542(70.1)		520(62.0) sh [d]	432(13.8)	375(83.0)	335(31.5)
γ-Co(en)(dpt)Cl^{2+} [b]	543(47.0)sh		484(59.4)	422(21.1)		
α-Co(tetren)Cl^{2+} [c]	522(109)		480(105) sh	417(37.5)	362(103)	328(43.6)
β-Co(tetren)Cl^{2+} [c]	525(98.6)	508(97.3)	480(101)	415(37.2)	360(107)	332(64.5)
$Co(NH_3)_5Cl^{2+}$ [e]	534(50.1)		467(11.0) sh		364(46.8)	
α-Co(en)(dpt)Br^{2+} [b]	551(66.9)		486(42.9) sh	447(20.4)		
β-Co(en)(dpt)Br^{2+} [b]	564(63)		532(51) sh	437(10)		
γ-Co(en)(dpt)Br^{2+} [b]	548(65.7)	512(53.8)	485(55.5)	429(31.6)		
α-Co(tetren)Br^{2+} [c]	548(132)		480(100) sh	423(48.1)		
β-Co(tetren)Br^{2+} [c]	550(121)	495(97.8)	480(98.0)	422(46.5)		
$Co(NH_3)_5Br^{2+}$ [e]	552(57.6)		470(11.5) sh		310(831) sh	
α-Co(en)(dpt)I^{2+} [b]	615(84.6)		593(80.2) sh	536(59.6)		
β-Co(en)(dpt)I^{2+} [b]	606(96.7)			540(68.8)		
$Co(NH_3)_5I^{2+}$ [f]	581(79.5)			527(56)	383(269)	
β-Co(en)(dpt)$(NCS)^{2+}$ [b]	506(237)			427(69.7)	312(1634)	
γ-Co(en)(dpt)$(NCS)^{2+}$ [b]	478(171)			417(94.1)		
α-Co(tetren)$(NCS)^{2+}$ [c]	490(219)			415(50.8)		
β-Co(tetren)$(NCS)^{2+}$ [c]	487(318)			412(71.7)		
$Co(NH_3)_5(NCS)^{2+}$ [e]	497(186)			430(35.5)	357(39.8) sh	
α-Co(en)(dpt)N_3^{2+} [b]	525(342)			448(91.7)		
α-Co(tetren)N_3^{2+} [c]	508(490)			432(117)		
$Co(NH_3)_5N_3^{2+}$ [e]	519(257)					
β-Co(en)(dpt)$(NO_2)^{2+}$ [b]	468(133)			405(39.5)		
γ-Co(en)(dpt)$(NO_2)^{2+}$ [b]	462(143)			403(53.8)		
β-Co(tetren)$(NO_2)^{2+}$ [c]	460(207)			397(51.6)		
$Co(NH_3)_5(NO_2)^{2+}$ [e]	458(100)				325(1660)	
α-Co(en)(dpt)$(OH_2)^{3+}$ [b]	495(83.9)			412(20.2)	355(98.6)	318(39.8)
α-Co(tetren)$(OH_2)^{3+}$ [c]	472(122)			405(33.0)	350(85.3)	
$Co(NH_3)_5(OH_2)^{3+}$ [e]	485(48)				340	
α-Co(en)(dpt)$(OH)^{2+}$ [b]	510(112)			435(47.4)	372(118)	322(61.6)
α-Co(tetren)$(OH)^{2+}$ [c]	490(149)			417(51)	348(147)	
$Co(NH_3)_5OH^{2+}$ [e]	503(62.5)			425(20)	370(70.8)	360(69)

[a] Everywhere numbers inside parenthesis are the molar absorbancy indeces, a_M (extinction coefficients ε) in $M^{-1}cm^{-1}$. Wavelengths are in milimicrons. [b] This research; in 0.1 F $HClO_4$, except in 0.1 F NaOH for the hydroxo complex. [c] D. A. House and C. S. Garner, *Inorg. Chem.* 6, 272 (1967), [d] sh = shoulder, [e] For references see Table II in D. A. House and C. S. Garner., *Inorg. Chem.* 6, 272 (1967), [f] M. Linhard and M. Weigel, *Z. Anorg. Allgem. Chem.*, 266, 49 (1951).

means of establishing isomeric purity, but the main method of isomer characterisation has been through the infrared spectra.

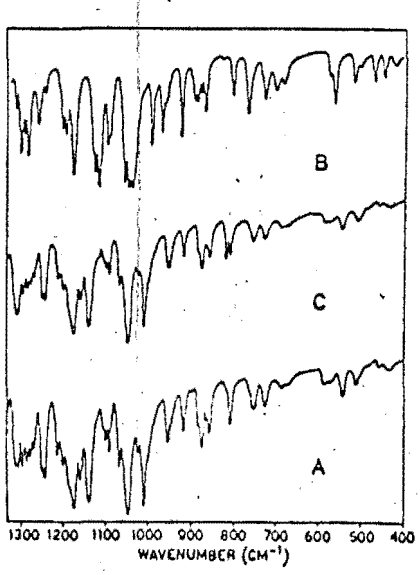

Figure 3. Infrared spectra of α, β and γ-[Co(en)(dpt)Cl]·$ZnCl_4$ in the 1300-400 cm^{-1} range (KBr disc.) A = α isomer, B = β isomer, C = γ isomer.

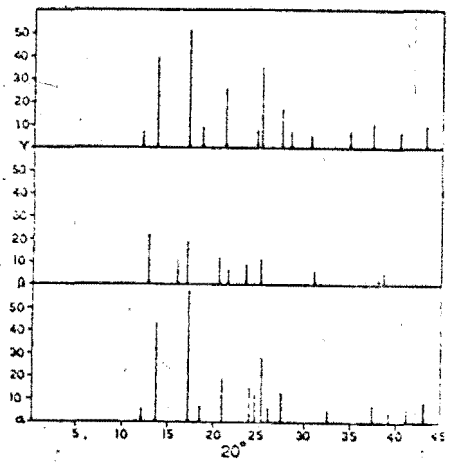

Figure 4. X-ray powder diffraction patterns of α, β and γ-[Co(en)(dpt)Cl]$ZnCl_4$ (2Θ = 4-45°). Vertical lines represent the positions and intensities (arbitary units) of the major peaks.

Figure 3 shows the infrared spectra of the α, β and γ chloro isomers, as the tetrachlorozincate(II) salts, in the 1300-400 cm^{-1} region. The infrared spectra of the other acido isomers show similar differences.

The α, β and γ-[Co(en)(dpt)Cl]$ZnCl_4$ salts also exhibit different X-ray powder diffraction patterns and Figure 4 schematically presents this data. The other acido isomers with a common anion show similar differences.

Discussion

Chemical Reactions: The α and β-chloro(ethylenediamine)(dipropylenetriamine)cobalt(III) tetrachlorozincate complexes described here are derived from the μ-peroxodicobalt(III) complex $[Co_2(en)_2(dpt)_2O_2](ClO_4)_4 \cdot 2H_2O$ [12] by decomposition of this in 30% HCl solution (3.6 F) containing zinc chloride.

The tetrachlorozincate anion has proved most useful, for these complexes, as the salts have satisfactory solubility properties, and this anion, unlike the perchlorate ion, is not infrared active in the 3500-400 cm^{-1} region. It does, however, have the disadvantage that for kinetic hydrolysis studies based on (halide) (halide titration measurements, of providing a high halide background, and perchlorate salts are more useful for this purpose.

The α chloro complex yields two isomeric nitro complexes (β and γ) on treatment with nitrous acid and these generate the β and γ chloro isomers with 12 F HCl. The β and γ chloro complexes generate only the β and γ nitro complexes respectively with nitrous acid. These reactions are summarised in Figure 5.

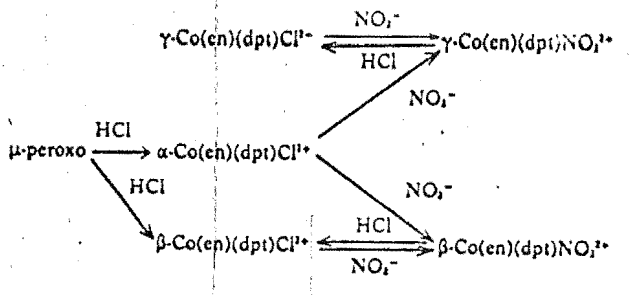

Figure 5. Isomeric interconversions for the α, β and γ chloro and nitro complexes.

Other acido complexes are prepared from the chloro isomers by conventional techniques.

Spectra: The most noticeable difference in the visible absorption spectra of the α, β and γ-Co(en)(dpt)Cl^{2+} cations (Table II, Figure 2) is that the α and β isomers have two bands in the 700-320 mμ region with a shoulder on the high wavelength band, while the γ isomer shows only the assymetric high wavelength band before the onset of charge transfer bands in the near ultraviolet region. This difference is ascribed to the different environment of the halide ligand in these complexes (Figure 1). The intensities at the band maxima of the acido(ethylenediamine)(dipropylenetriamine) complexes are intermediate between those of the corresponding acido pentammine and acidotetraethylenepentamine complexes, suggesting that the number of chelate rings may be influencing this parameter. In other respects, the spectra of the analogs in these three classes of complex are similar, as would be expected from the fact that in each class the chromophore is CoN_5X.

The infrared spectra of α, β and γ-[Co(en)(dpt)Cl]$ZnCl_4$ in the 1500-400 cm^{-1} region (KBr disc) are shown in Figure 3. The α and γ forms have very similar spectra in this region apart from the characteristic γ doublet at about 820 cm^{-1}, while the spectrum of the β isomer shows many differences from the spectra of the γ and α forms. In addition, the α and γ-[Co(en)(dpt)Cl]$ZnCl_4$ isomers show two broad bands at about 3200 cm^{-1} (due to NH_2 stretch) and a singlet band at about 1580 cm^{-1} (NH_2 bend). In the β form, the 3200 cm^{-1} bands are resolved into four and the 1580 cm^{-1} band is split into a triplet. These splittings in the infrared spectra are characteristic of all the acido β salts isolated and together with the 820 cm^{-1} γ doublet served to detect the presence of isomeric mixtures in any particular preparation. The spectra of synthetic mixtures of the pure isomers show that from the infrared spectrum it is possible to detect 5-10% of one isomer in the presence of the other.

The differences in the infrared spectra are ascribed to the different geometric arangements of the polyamine ligands about the central metal ion (Figure 1) causing different ring vibrations and hydrogen bond effects. Similar differences in the infrared spectra of Co(tetren)X^{n+} [3,4] and M(trien)X_2^{n+} [13,14] isomers have also been observed.

The infrared spectra of the bromo and iodo tetrachlorozincate salts are very similar to their chloro analogs but those of the nitro, isothiocyanato and azido tetrachlorozincate salts show bands characteristic of the acido ligand and these sometimes obscured the bands used for isomeric assignment. If such were the case, these acido complexes were converted to the chloro isomers and the infrared spectra of the tetrachlorozincate salts used for isomer identification.

The positions of the $-NO_2$ bands in the β and γ-[Co(en)(dpt)NO_2]X_2 salts showed that these were nitro rather than the isomeric nitrito complexes.

Geometric Configurations: Assuming that these isomers are related by the successive edgewise displacement of amine groups in the order I, II and III in Figure 1, the only configuration that could produce two different isomeric forms in a single displacement process would be II. That is, displacement of $-NH_2$ in ethylenediamine to give III or displacement of $-NH_2$ in dipropylenetriamine to give I. On this basis we assign the α chloro isomer to configuration II, as this form gives a mixture of the β and γ nitro isomers. We can rule out a series of successive displacements *e.g.* I→II→III or III→II→I as, if this were the case, some reversibility in the system between II and III (or II and I) would be expected. This has not been observed and the β and γ chloro

(12) The properties of this and other brown diamagnetic μ-peroxo and green paramagnetic μ-superoxo polyaminecobalt (III) complexes will be described subsequently.

(13) D. A. Buckingham and D. Jones, *Inorg. Chem.*, *4*, 1387 (1965).
(14) D. A. House and C. S. Garner, *J. Am. Chem. Soc.*, *88*, 2156 (1966).

isomers give *only* the β and γ nitro isomers respectively. (Figure 5).

In addition, configuration II is the only potentially optically active system of the three configurations. Unfortunately we have not been able to resolve the α-[Co(en)(dpt)Cl]$ZnCl_4$ salt using potassium *d*-antimony(III) oxytartrate but this in no way indicates that this compound is optically inactive, and other resolving agents are being tried.

We further suggest that the γ and β isomers correspond to configurations III and I (Figure 1) respectively. The variations in the infrared spectra of these isomeric forms are believed to be primarily due to the various arrangements of the polyamine ligands about the central metal ion. The spectra of the α and γ forms are very similar (Figure 3) and as the polyamine arrangement in configurations II and III are also very similar (Figure 1), the γ form is assigned to configuration III. On the other hand, the variations in the visible absorption spectra are believed to be due to the different environments of the halide ligand in the complex ion. The absorption spectra of the α and β forms are similar (Figure 2), in contrast to that of the γ isomer, and as the position of the halide ligand in configurations I and II are also similar (*trans* to a primary amine group in each case) we believe configuration I to correspond to the β form.

Up till now we have made mention of conformational isomers that could arise due to the *cis* or *trans* position of the coordinated secondary amine hydrogen atom. The techniques we have used here would not be expected to detect such isomerism, and optical activity, used to detect similar isomerism in N-methylethylenediamine[15] and triethylenetetramine[7] cobalt(III) complexes cannot be used as the coordinated secondary amine in the dipropylenetriamine ligand is not assymetric.

Preliminary data on the rate of base hydrolysis[16] of the α, β and γ-Co(en)(dpt)Cl^{2+} cations, does however, suggest that conformational isomers are present in these systems.

The rate data can be resolved into two components for each isomer and the rate ratios k_{fast}/k_{slow} are almost constant for the three isomeric systems.

The different rate detectable components could arise from either twinned crystals, crystal mixtures, or a rapidly established equilibrium mixture when the conformationally pure isomer is dissolved. Work is in progress to understand this problem more fully.

Acknowledgements: We thank Professor A. G. McLellan of the Department of Physics, University of Canterbury, for the use of the Cary 14 spectrophotometer and Dr W. Oldershaw of the Department of Geology, University of Canterbury for the use of the X-ray powder diffraction apparatus. We also thank Dr D. A. Buckingham and Mr M. Dwyer of the Australian National University, Canberra, for optical rotatory dispersion measurements.

(15) D. A. Buckingham, L. G. Marzilli and A. M. Sargeson, *Inorg. Chem.*, 7, 915 (1968) and the references cited therein.
(16) R. W. Hay and coworkers, Victoria University of Wellington, New Zealand, personal communication.

Contribution from the Department of Chemistry, University of Canterbury, Christchurch, New Zealand

Acidopentaminecobalt(III) Complexes with Polyamine Ligands. II. The Four Geometric Isomers of the Chloro(ethylenediamine)(diethylenetriamine)cobalt(III) Ion [1]

A. R. Gainsford and D. A. House

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Tetrachlorozincate(II) salts of the four (ω, ϰ, π and ε) possible geometric isomers of the Co(en)(dien)Cl²⁺ have been synthesised. The π and ε forms contain the dien ligand in the facial (cis) configuration with the cloro ligand trans to the NH₂ and NH groups of the dien respectively. The ω and ϰ forms contain the dien ligand in the peripherial (trans) configuration with the NH hydrogen of the dien ligand adjacent to and remote from the chloro ligand, respectively. Chemical interconversions of the isomers and their infrared and visible absorption spectra are described.

Introduction

As part of a continuing investigation of acidopentaminecobalt(III) complexes with mixed diamine-triamine ligands, we describe here the preparation, properties, stereochemistry and interconversions of the four possible isomers of the Co(en)(dien)Cl²⁺ ion.[2]

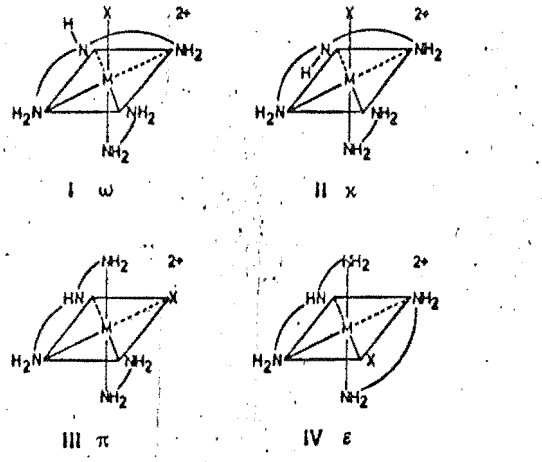

Figure 1. Possible geometric isomers of the Co(en)(dien)X²⁺ ion (X = Cl).

(1) Part I, *Inorg. Chim. Acta*, *3*, 33 (1969).
(2) Abbreviations used: en = $NH_2(CH_2)_2NH_2$, dien = $NH_2(CH_2)_2NH(CH_2)_2NH_2$, dpt = $NH_2(CH_2)_3NH(CH_2)_3NH_2$, tetren = $NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$.
(3) R. G. Pearson, C. R. Boston, and F. Basolo, *J. Phys. Chem.*, *59*, 304 (1955).
(4) G. G. Schlessinger, *Gannon Coll. Chem. J.*, *2*, 20 (1965).
(5) B. Bosnich and F. P. Dwyer, *Aust. J. Chem.*, *19*, 2045 (1966).
(6) B. Bosnich and F. P. Dwyer, *Aust. J. Chem.*, *19*, 2051 (1966).

Salts of the Co(en)(dien)Cl²⁺ ion have been described previously[3-6] but only in the case of Bosnich and Dwyer's work[5] was there more than one (*viz.* two) isomer detected.

Using a variety of synthetic methods, we have prepared tetrachlorozincate(II) salts of the four Co(en)(dien)Cl²⁺ isomers and have assigned them to the configurations shown in Figure 1.

The ω and ϰ isomers can be regarded as *cis* and *trans* forms differing only in the position of the NH proton. The π, ϰ and ε isomers are related by edgewise displacements of the dien and en respectively.

Experimental Section

The commercial amines were used without further purification. All other chemicals were of reagent grade quality. $[Co_2(en)_2(dien)_2O_2](ClO_4)_4 \cdot 2H_2O$,[7] $Na_3[Co(CO_3)_3] \cdot 3H_2O$[8] and *trans*–$Co(dien)(NO_2)_3$[5,9] were prepared by the literature methods. Infrared spectra of the $ZnCl_4^{2-}$ salts were used to determine the isomeric composition of the chloro complexes.

Isomers of Chloro(ethylenediamine)(diethylenetriamine)cobalt(III) Tetrachlorozincate(II). Method A: $[Co_2(en)_2(dien)_2O_2](ClO_4)_4 \cdot 2H_2O$ (30 g) was added to a solution of 12 F HCl (85 ml) in water (170 ml) containing $ZnCl_2$ (50 g). The solution was heated on a steam bath (ca. 80°) until the effervescence ceased (0.5 hr) during which time a red crystalline material was deposited. The solution was cooled to room temperature and the product was collected, washed with 2-propanol and then ether; yield 13 g. The crude product was recrystallised by dissolving it in the minimum volume of 0.2 F HCl at 50° (ca. 150 ml) and then adding 12 F HCl (50 ml) and $ZnCl_2$ (25 g). The product from the cooled solution was collected and washed as above. Losses were mechanical and the product was a π–ϰ mixture in a 42% yield.

The original mother liquor (orange-brown) was again heated at 80° and after 0.5 hr a further 50 ml portion of 12 F HCl was added to the solution. An orange-red product slowly deposited and this was

(7) D. L. Duffy, D. A. House, and J. A. Weil, *J. Inorg. Nucl. Chem.*, in press.
(8) H. F. Bauer and W. C. Drinkard, *J. Am. Chem. Soc.*, *82*, 5031 (1960).
(9) P. H. Crayton, *Inorg. Synth.*, *7*, 211 (1963).

collected and washed as above. The product was recrystallised as above but using a corresponding reduction in volumes and weights of reagents. The yield was 1.5 g of the pure x isomer. The total yield of chloropentamine complex was 47%.

Method B. $Co(dien)(NO_2)_3$[9] (15 g) was suspended in water (30 ml) and ethylenediamine (3.3 ml, 100%) was added. The solution was stirred and allowed to digest on a steam bath for 1 hr. The filtered solution was heated to 80° and 12 F HCl (30 ml) was cautiously added. Heating was continued for a further hour, during which time the evolution of nitrogen oxides subsided, and a deep red color was produced. $ZnCl_2$ (15 g) and 12 F HCl (5 ml) were then added and after heating for a further 30 min, the product commenced to crystallise. The product was collected in about 2g fractions, which were washed with 2-propanol and ether. Each fraction was recrystallised by dissolving the crude complex in the minimum volume of 0.2 F HCl at 25° (1 g/50 ml) and then adding 12 F HCl (25 ml/1 g) and $ZnCl_2$ (5 g/1 g). The products were again collected in fractions and were collected and washed as above. The isomeric composition of the fractions are tabulated below.

Crude Crop No.	Recrytallised Crop No.	Isomeric Composition	Yield (g) of Recrytallised Product
1	1, 2, and 3	ε	2.3
2	1 and 2	ε	2.3
3	1	ω	0.6
	2	ω+ε	0.5
4	1	ε+x	0.6
	2	ε+ω+x	0.7
	3	ε+x	0.7

The total yield was 7.7 g or 36% and fractions after the 4th crop increasingly contaminated with yellow hexamine salts.

Method C. The procedure of Bosnich and Dwyer[5] was followed on a 1/20 scale. The crude product was converted to the tetrachlorozincate(II) salt by dissolving it in the minimum volume of 50° 0.1 F HCl and then adding excess 12 F HCl and $ZnCl_2$. The material that deposited on cooling in an ice bath was collected in fractions, washed with 2-propanol and then ether (Crops 1-4). The original mother liquor was heated to 50° and 10 g of $ZnCl_2$ in 20 ml of 12 F HCl was added. The product that deposited was collected in fractions and recrystallised as above (Crops 5-7). The total yield was 12.4 g ,63%). The 1st, 2nd and 3rd crops were the pure ω isomer (6.5 g), the 4th crop an ε-ω mixture, the 5th and 6th crops a π–x mixture and the 7th crop consisted of the x isomer contaminated with hexamine impurities.

Method D. $CoCl_2 . 6H_2O$ (7 g), NH_4Cl (25 g) and NH_4I (0.5 g) were added to 40 ml of water and I_2 (3.7 g) dissolved in 80 ml of ethanol was added to the stirred aqueous suspension. This was followed by the addition of ethlylenediamine (2.1 ml) and diethylenetriamine (3.4 ml) in 20 ml of water. The mixture was stirred at room temperature for 3 hr, during which time a deep red color developed. The solution was allowed to stand overnight when red needles along with some NH_4Cl were deposited. The crude product was converted to the $ZnCl_4^{2-}$ salt as in Method C. Two further crops were obtained by addition of acetone and methanol (150 ml of a 1:1 mixture) after filtration of the precipitated ammonium salts and these were converted to the $ZnCl_4^{2-}$ salt. A total yield of 0.8 g of the pure ω isomer was obtained. Finally, the mother liquor (450 ml) was evaporated on a steam bath to 250 ml and 15 g of $ZnCl_2$ in 50 ml of 12 F HCl was added. The red product that deposited from the ice cold solution was collected in 1-2 g fractions. These were washed with 2-propanol and ether and recrystallised as above. The three crops that were collected consisted of a π–x mixture and the third crop also contained some ω isomer. The total yield was 6 g or 45%.

Method E. Freshly prepared $Na_3[Co(CO_3)_3] . 3H_2O$[8] (10 g) was suspended in 30 ml of water and a mixture of ethylenediamine (2.15 ml) and diethylenetriamine (4.95 ml) was added. After heating at 80° for 15 min, 12 F HCl (20 ml) and $ZnCl_2$ (10 g) were cautiously added to the now red solution. Successive crystal crops were collected over a period of several days and were recrystallised as in Method A. Crops one and two (0.5 g each) consisted of the π isomer and the third crop was a π-ω-x mixture (0.6 g). Subsequent crops were contaminated with hexamine salts. The yield of the chloropentamine complex was only 9%.

Analysis. Analytical data for the pure isomers (infrared spectra) are: Calcd. for $[Co(en)(dien)Cl]ZnCl_4$: C, 15.5; H, 4.55; N, 15.0; Co, 12.7; Cl, 38.2%. Found: ω isomer C, 15.9 H, 4.56 N, 14.9 Co, 12.6 Cl, 37.8: x isomer C, 15.7 H, 4.59 N, 14.9 Co, 12.6 Cl, 38.1: π isomer C, 15.8 H, 4.64 N, 15.1 Co, 12.6 Cl, 38.1: ε isomer C, 15.8 H, 4.48 N, 15.4 Co, 12.5 Cl, 37.9%.

Separation of a π-x Mixture. Method 1. The mixture of the π-x isomers (generated by Method A, ca. 35% x was dissolved in 0.2 F $HClO_4$ (15 g, 150 ml) and twice the weight of solid $NaClO_4 . H_2O$ was stirred in. Pure x–$[Co(en)(dien)Cl](ClO_4)_2$ (5 g) was deposited immediately and this was collected, washed with 2-propanol and the ether. $ZnCl_2$ (20 g) in 12 F HCl (50 ml) was added to the mother liquor and the pure or partly purified π–$[Co(en)(dien)Cl]ZnCl_4$ was precipitated. This was recrystallised as described previously in Method A. x–$[Co(en)(dien)Cl]ZnCl_4$ was made from the perchlorate salt by dissolving the latter in water (5 g, 50 ml) and adding 12 F HCl (25 ml) and $ZnCl_2$ (10 g). The precipitated product was collected, washed and dried as above. Losses in this procedure were mechanical.

Method 2. The π-x isomeric mixture (20 g) generated by Method A, was dissolved in water (150 ml) and a solution of KOH (20 g) in water (50 ml) was added. The solution was heated at 60° for 20 min, filtered, cooled in ice, and ice cold 12 F HCl (350 ml) containing $ZnCl_2$ (20 g) was added dropwise. The orange colored solution was set aside at room temperature and after 2 days, the first crystal crop

(3 g pure π–[Co(en)(dien)Cl]$ZnCl_4$) was collected, washed with 2-propanol then ether and air dried. Subsequent crops were again π-x mixtures (14 g).

Qualitative Isomerisation Reactions. Small quantities of the pure isomers were taken and subjected to the following chemical reactions. The isomeric composition of the chloro $ZnCl_4^{2-}$ product was determined by examination of the infrared spectrum.

(*a*) *Base Hydrolysis.* The π, ε, ω and x isomers of [Co(en)(dien)Cl]$ZnCl_4$ were separately dissolved in water (0.25 g, 15 ml, 0.25g, 15 ml, 0.1 g, 15 ml and 0.25 g, 15 ml respectively) and ca. 10 ml of 1 F NaOH was added until all the $Zn(OH)_2$ had precipitated. The solutions were heated at 70° for 20 min and then 4 g of $ZnCl_2$ in 10 ml of 12 F HCl was added. The solutions were left to stand at room temperature overnight and the product was collected, washed with 2-propanol and then ether. The results were: ω→π+x; ε→π; x→π+x; π→π.

(*b*) *Reflux in 6 F HCl.* The pure isomers of [Co(en)(dien)Cl]$ZnCl_4$ were separately dissolved in 6 F HCl (0.2 g/25 ml) and the solutions were boiled under reflux for 1 hr. Concentrated HCl (15 ml, 12 F) containing $ZnCl_2$ (5 g) was added and the products that deposited from the ice cooled solutions were collected. The results were: x→x; π→π; ω→ω; ε→π.

(*c*) *Refluxed in 0.05 F HCl.* Similar amounts and conditions were used as in (b) except that the 6 F HCl was replaced by 0.05 F HCl. The results were: ε→π+x+ε; x→x+π; π→π+x; ω→ω.

(*d*) *Reaction with Nitrous Acid.* Nitro compounds derived from the π, x, ε and ω–[Co(en)(dien)Cl]$ZnCl_4$ isomers were prepared using a method to be described in a later publication. These were decomposed by heating (80°) a solution of each in 3 F HCl for one hr. The $ZnCl_4^{2-}$ salts of the chloro isomers generated in this manner were deposited by the addition of $ZnCl_2$. The transformations that resulted were: π→ε; x→x; ε→ε; ω→ω.

Perchlorate Salts. One half gramme of the isomerically pure [Co(en)(dien)Cl]$ZnCl_4$ salts were dissolved in the minimum volume of 80° 3 F $HClO_4$ (25-30 ml) and excess $NaClO_4 . H_2O$ (*ca.* 5 g) was added. The products that crystallised from the ice cooled solutions were collected, washed with 2-propanol, then ether and air dried. The ε and π isomers crystallised as the diperchlorate monohydrates, the x isomer as the diperchlorate and the ω isomer as the chloride-perchlorate salt. The yields were: ε, 49%; π, 55%; x, 53% and ω, 53%.

Anal. Calcd. for [Co(en)(dien)Cl]$(ClO_4)_2 . H_2O$: C, 15.18; H, 4.88; N, 14.75; Co, 12.41; Cl (non-perchlorate) 7.47. Found: ε isomer; C, 15.39; H, 4.99; N, 15.08; Co, 11.99; Cl, 7.51: π isomer; C, 15.09; H, 4.96; Co, 12.44; Cl, 7.85. Calcd. for [Co(en)(dien)Cl]$(ClO_4)_2$: C, 15.78; H, 4.64; N, 15.34; Co, 12.91; Cl (non-perchlorate), 7.77. Found: x isomer; C, 15.75; H, 4.72; N, 14.96; Co, 12.85; Cl, 7.71. Calcd. for [Co(en)(dien)Cl]$(ClO_4)Cl$: C, 18.35; H, 5.39; N, 17.84; Co, 15.01; Cl (non-perchlorate), 18.06. Found: ω isomer; C, 18.46; H, 5.51; N, 17.61; Co, 15.50; Cl, 18.25.

Anal. Co and Cl were determined as described previously.[1] C, H and N analyses were performed by Dr A. D. Campbell of the University of Otago, New Zealand.

Spectral Measurements. The visible absorption spectra were obtained with a Cary 14 recording spectrophotometer using matched 1 cm quartz cells. Spectrophotometric analyses for Co were performed using a Beckman DBG recording spectrophotometer. The infrared spectra were determined in both mulls and KBr discs using a Perkin Elmer 337 or a Shimadzu IR-27 G infrared spectrophotometer.

Results

The four isomers (ω, ε, π and x) of [Co(en)(dien)Cl]$ZnCl_4$ have been prepared and structural assignments made according to Figure 1. The infrared spectra of these salts (1700-400 cm^{-1} range) (KBr discs) are shown in Figure 2 and the visible absorption spectra (0.1 F $HClO_4$) of the isomeric cations are shown in Figure 3. Spectral parameters for the Co(en)(dien)Cl^{2+} and Co(en)(dien)OH_2^{3+} ions are listed in Table I, together with similar data for α and β–Co(tetren)Cl^{2+} and α–Co(tetren)OH_2^{3+}.[10-12] The a_M values for the various Co(en)(dien)Cl^{2+} isomers were within 3% for different preparations of the $ZnCl_4^{2-}$ salts with similar infrared spectra characteristic of that particular isomer.

The isomeric aquo cations were generated in solution from the chloro analogs by addition of Hg^{2+} (as the acetate salt) in 0.1 F $HClO_4$. The rates of color change (red → orange) at room temperature were in the order ε > π > x ~ ω and the Hg^{2+} catalysed hydrolysis was complete for all isomers after 18 hr as evidenced by constant and reproducible spectral parameters. Identical aquo cations were also generated from the chloro isomers by addition of base (0.1 F NaOH) and acidification with 0.3 F $HClO_4$ after 5 min at room temperature.

Discussion

Synthetic Methods. The amount of any particular Co(en)(dien)Cl^{2+} isomer is markedly dependent upon the method of synthesis. The reaction between *trans*-Co(dien)$(NO_2)_2$[13] gives, presumably, a mixture of the Co(en)(dien)NO_2^{2+} isomers which form nitro complexes (ω, x and ε), as the corresponding chloro isomers are isolated as the $ZnCl_4^{2-}$ salts by treating the solution with HCl/$ZnCl_2$. The π chloro isomer cannot be formed directly in this synthesis as treatment of π-Co(en)(dien)Cl^{2+} with HNO_2 produces ε-Co(en)(dien)-NO_2^{2+}. The formation of the π chloro isomer in small

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Table I. Visible Absorption Maxima and Minima for ω, ε, π and χ—Co(en)(dien)Cl^{2+}; ω, ε, π and χ—Co(en)(dien)OH_2^{3+}; α and β—Co(tetren)Cl^{2+} and α—Co(tetren)OH_2^{3+} in 0.1 F $HClO_4$ at 20-25° [a,b]

Complex	min	max	min	max	min	max
ω—Co(en)(dien)Cl^{2+}	323	358	416	480 sh		532
	(75.0)	(100.8)	(19.3)	(60)		(92.0)
ε—Co(en)(dien)Cl^{2+}		314 sh	405	463	485	522
		(346)	(20.8)	(55.9)	(50.7)	(53.9)
π—Co(en)(dien)Cl^{2+}	326	361	412	475 sh		525
	(33.6)	(71.0)	(15.0)	(44)		(67.0)
χ—Co(en)(dien)Cl^{2+}	332	366	416	488 sh		515
	(35.2)	(87.9)	(30.3)	(84)		(85.6)
α—Co(tetren)Cl^{2+}	328	362	417	480 sh		522
	(43.6)	(103)	(37.5)	(105)		(109)
β—Co(tetren)Cl^{2+}	332	360	415	480	508	525
	(64.5)	(107)	(37.2)	(101)	(97.3)	(98.6)
ω—Co(en)(dien)OH_2^{3+}	300	342	398	487		
	(30.3)	(86.2)	(17.0)	(72.1)		
ε—Co(en)(dien)OH_2^{3+}		324	384	436		
		(332)	(24.4)	(79.5)		
π—Co(en)(dien)OH_2^{3+}	303	346	397	476		
	(20.5)	(71.0)	(21.0)	(78.5)		
χ—Co(en)(dien)OH_2^{3+}	304	361	402	473		
	(22.2)	(80.2)	(27.4)	(99.5)		
α—Co(tetren)OH_2^{3+}		350	405	472		
		(85.3)	(35.0)	(122)		

[a] Everywhere, numbers inside parenthesis are the molar absorbancy indeces, a_M (extinction coefficients, ε) in M^{-1} cm^{-1}. Wavelengths are in nanometers (millimicrons). [b] Data for the Co(tetren)X^{n+} cations are from references 10-12.

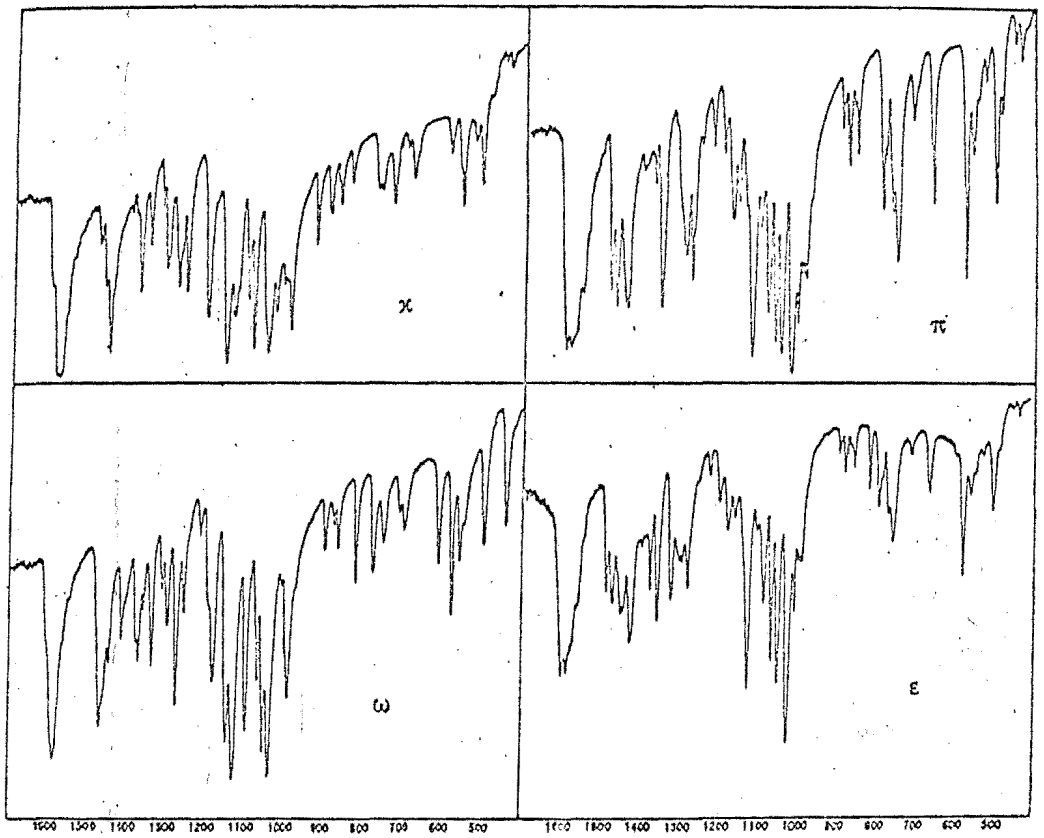

Figure 2. Infrared spectra of ω, ε, π and χ—[Co(en)(dien)Cl]$ZnCl_4$ in the 1700-400 cm^{-1} range (KBr disc).

amounts, presumably arises via isomeric conversion of the ε chloro isomer, which has been shown to transform to the π chloro form in refluxing 6 F HCl. The above method of synthesis was originally used by Bosnich and Dwyer[5] who isolated the ω chloro chloride as the major product from the nitro intermediates after treatment with 12 F HCl. They tentatively assigned this form to either configurations III or IV (Figure 1), but from evidence presented later, we suggest that the ω isomer has configuration I. A minor component was also isolated and from the visible absorption spectrum, this appears to be the chloro

chloride of our x isomer. The chloride salts of the ε and π isomers are apparently too soluble to be isolated by this method. The use of the larger tetrachlorozincate(II) ion, does however, allow their isolation using this route.

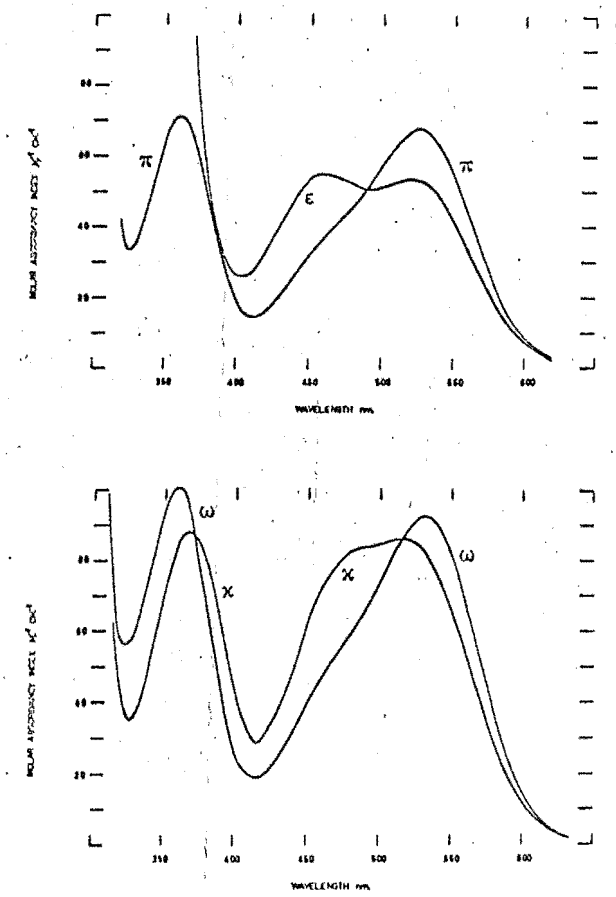

Figure 3. Visible absorption spectra of ω, ε, π and χ—Co(en)(dien)Cl^{2+} in 0.1 F $HClO_4$ at 20-25°.

Decomposition of $Co_2(en)_2(dien)_2O_2^{4+}$ [7] with HCl containing $ZnCl_2$ forms only the $ZnCl_4^{2-}$ salts of the π and χ chloro isomers.[14] It is possible that $Co_2(en)_2(dien)_2O_2^{4+}$ contains both the π and χ arrangements of the ligands and we are currently trying to detect isomeric mixture in μ peroxo polyamine complexes of this type.[7] A more likely explanation is that the μ peroxo complex contains only one polyamine configuration and that the aquo intermediate originally produced in the decomposition, forms a π—χ equilibrium mixture. Support for this latter hypothesis comes from the fact that refluxing χ—[Co(en)(dien)Cl]$ZnCl_4$ in 0.05 F HCl for one hr and adding 12 F HCl results in about 30% conversion to the π chloro isomer.

$Na_3Co(CO_3)_3 \cdot 3H_2O$[8] reacts with an en/dien mixture forming mixtures of the π—χ chloro isomers on acidification with $HCl/ZnCl_2$, but the yields are low and considerable amounts of hexamine products are produced. An attempt was made to prepare [Co(en)(dien)I]Cl_2 using the method of Yalman[15] for the formation of the ammine analog. However, ω—[Co(en)(dien)Cl]Cl_2 was deposited, and when the solution was acidified with $HCl/ZnCl_2$, mixtures of the π and χ chloro isomers were isolated.

Several methods were found to interconvert the isomers and these were investigated qualitativly. Treatment of the pure ω, ε and χ chloro isomers with excess hot NaOH solution and reacidification with HCl to form the chloro $ZnCl_4^{2-}$ salts resulted in conversion to a mixture of the π and χ forms. It is probable that the π and χ hydroxo (or aquo) ions form an equilibrium mixture which gives the chloro mixture on anation. Mention has already been made of the π⟶ε isomerisation via the nitro complex and the ε⟶π rearrangement in refluxing 6 F HCl.

It is difficult to generalise from these data, but it appears probable that the π and χ isomer result from the formation of Co^{II} or Co^{III} hydroxo complexes and that the ω, ε and χ isomers can form when the synthetic route does not involve these intermediates.

Spectra. The most noticeable difference between the four isomers of [Co(en)(dien)Cl]$ZnCl_4$ is in the infrared spectrum (Figure 2). Even here, however, there are often only one or two significant bands that allow isomer differentiation. In particular, the bands that serve to distinguish the χ, ε and ω isomeres, respectively, from each other and from π are χ, 930; ε, 820, 661 and ω, 820, 610 cm^{-1}. The infrared spectrum have also been used as an index of purity for any particular isomer. The spectra of synthetic mixtures of the pure isomers show that it is possible to detect 5-10% of one isomer in the presence of the other. Nevertheless, care must be taken in the interpretation of the infrared spectrum, as fractional crystallisation does not always lead to isomer separation especially with π and χ—[Co(en)(dien)Cl]$ZnCl_4$ mixtures. The separation of this particular mixture is best effected by fractional crystallisation as the perchlorate salts, when χ—[Co(en)(dien)Cl]$(ClO_4)_2$ crystallises first, followed by the $ZnCl_4^{2-}$ salt of the π isomer.

The visible absorption spectra of the π, χ and ω chloro isomers are quite similar (Figure 3) showing two well defined maxima at about 360 and 520 nm. The 520 nm bands are broad and exhibit a shoulder on the low wavelength side which becomes more pronounced in the order ω<π<χ. The ε chloro isomer exhibits only the 520 nm maxima of comparable intensity but here the band is split into two well resolved maxima. In addition there is a high intensity (a_M = 346) shoulder at 314 nm (not shown in Figure 3) on the high wavelength side of the charge transfer bands in the ultraviolet.

Thus the spectra of these Co(en)(dien)Cl^{2+} isomers are similar to those of the Co(en)(dpt)Cl^{2+} [1] and Co(tetren)Cl^{2+} [10-12] isomers. Such similarity is expected as these systems all contain the CoN_5Cl^{2+} chromophore.

All four aquo isomers exhibit two bands in the 300-700 nm region, however, the maxima for the ε aquo isomer are shifted about 10 nm to lower wavelengths and the low wavelength maxima is of much greater intensity than for the comparable band in the other forms.

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Structural Assignments. Consideration of the structures I-IV (Figure 1) suggest that the configurations II-IV should form an interconvertable system via edgewise displacement of the dien or en ligands. Such displacements in structures I cannot take place because of the position of the NH proton. This implies that the isomer corresponding to I should not rearrange under conditions where the NH proton remains intact. Rearrangement is possible, however, if the NH proton were removed such as in an S_N 1CB base hydrolysis mechanism.[16]

We are currently investigating this and related systems to see if such rearrangements can provide evidence to support the S_N1CB mechanism.

Structures I and II can be regarded as *cis* and *trans* NH forms and similarly related configurations have been postulated in the *trans*—(O-X)-Co(dien)(gly)X^+ (X = CN) system[17] where two distinct forms were detected in solution by nuclear magnetic resonance.

Of the structures I-IV, only III is potentially optically active. Unfortunately we have not been able to resolve any of the chloro isomers described here and the property of optical activity cannot, at present, be used for structural assignments.

The structural pairs I-II and III-IV contain the dien ligand in the peripherial (*trans*) and facial (*cis*) configurations, respectively. Previous workers[18-20] have used infrared spectral data to assign the configuration of the dien ligand in monodiethylenetriamine complexes. Of particular significance are the bands in the 800-950 cm^{-1} region where the *cis* and *trans* monodiethylenetriamine complexes have 3 and 4 bands respectively. Using this criterion for the assignment of the dien ligand, the infrared spectra of the [Co(en)(dien)Cl]$ZnCl_4$ isomers (Figure 2) suggest that the ω and χ forms have the *trans* arrangement and the π and ε isomers the *cis* form, assuming the en ligand has little influence on the spectra in the 800-950 cm^{-1} region. In the infrared spectrum of monoethylenediamine complexes such as $Co(en)(NH_3)(NO_2)_3$ and [Co(en)$(NH_3)(OH_2)Cl_2$]Cl, there are two weak bands at 880 and 900 cm^{-1} due to the en and these probably appear as low intensity shoulders on the dien bands of the [Co(en)(dien)Cl]$ZnCl_4$ isomers.

Of the four chloro isomers isolated, only the π chloro form has been found to give two different isomers by chemical conversion. Thus, treatment with HNO_2 yields the ε nitro isomer and on refluxing with 0.05 F HCl, followed by the addition of 12 F HCl, there is partial conversion to the χ chloro. This suggests that the π chloro has the configuration III, as it is this form which would be expected to give rise to two different products via displacement of the dien (configuration II) or the en (configuration IV). If this is the case, the behaviour of the π chloro isomer is slightly different from the analogous α–Co(en)(dpt)Cl^{2+} [1] with configuration III, which gives a mixture of two nitro complexes, corresponding to configurations II and IV, on treatment with HNO_2.

The similarity of the infrared spectrum of the π chloro isomer with that of the ε chloro form suggests that the ε form corresponds to IV, with the acido ligand now *trans* to the coordinated secondary amine group and the dien remaining in the 1, 2, 3 configuration. The assignment of configuration IV to the analogous γ–Co(en)(dpt)Cl^{+2} [1] was based on similar evidence. In addition, the visible absorption spectra of the ε–Co(en)(dien)Cl^{2+} and γ–Co(en)dpt)Cl^{2+} [1] ions are very similar, and different from the other isomers in their respective series, again suggesting similar geometries for these forms.

Acido ligands *trans* to coordinated secondary amine groups are known to aquate more rapidly than those *trans* to primary amine groups.[21] This provides further support for the assignment of the ε chloro isomer to configuration IV, as it is this form which exhibits the greatest rate of reaction with Hg^{2+} in $HClO_4$. The uncatalysed aquation rates for these chloro isomers are now under investigation.

The assignment of the χ chloro isomer to configuration II is based on the observation that this form is converted to the π chloro isomer under both acid alkaline conditions (*i.e.* via both the aquo and hydroxo intermediates). The ω chloro form is converted to the π chloro isomer only via base hydrolysis and is particularly stable in all other respects to isomer interconversion. Hence the ω isomer is assigned to configuration I.

The magnitude of the rate constants for the base hydrolyses of the three chloro isomers that have been measured[22] are in the order π>χ>ω with a rate ratio of 10^4:5:1 respectively. Similar variations in the magnitude of the rates of base hydrolysis have also been observed in the four Co(tetren)Cl^{2+} isomers.[23]

Bosnich and Dwyer[6] have measured the hydrolysis rates of the two Co(en)(dien)Cl^{2+} isomers they isolated (apparently our ω and χ) in 0.01 F $HClO_4$. Their results show that the χ chloro isomer hydrolyses approximately 2.3 times faster than the ω isomer at this acidity. Such a rate difference would be expected as the released halide is *trans* to a primary group in both complexes, if they have configurations II and I respectively, as we propose.

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